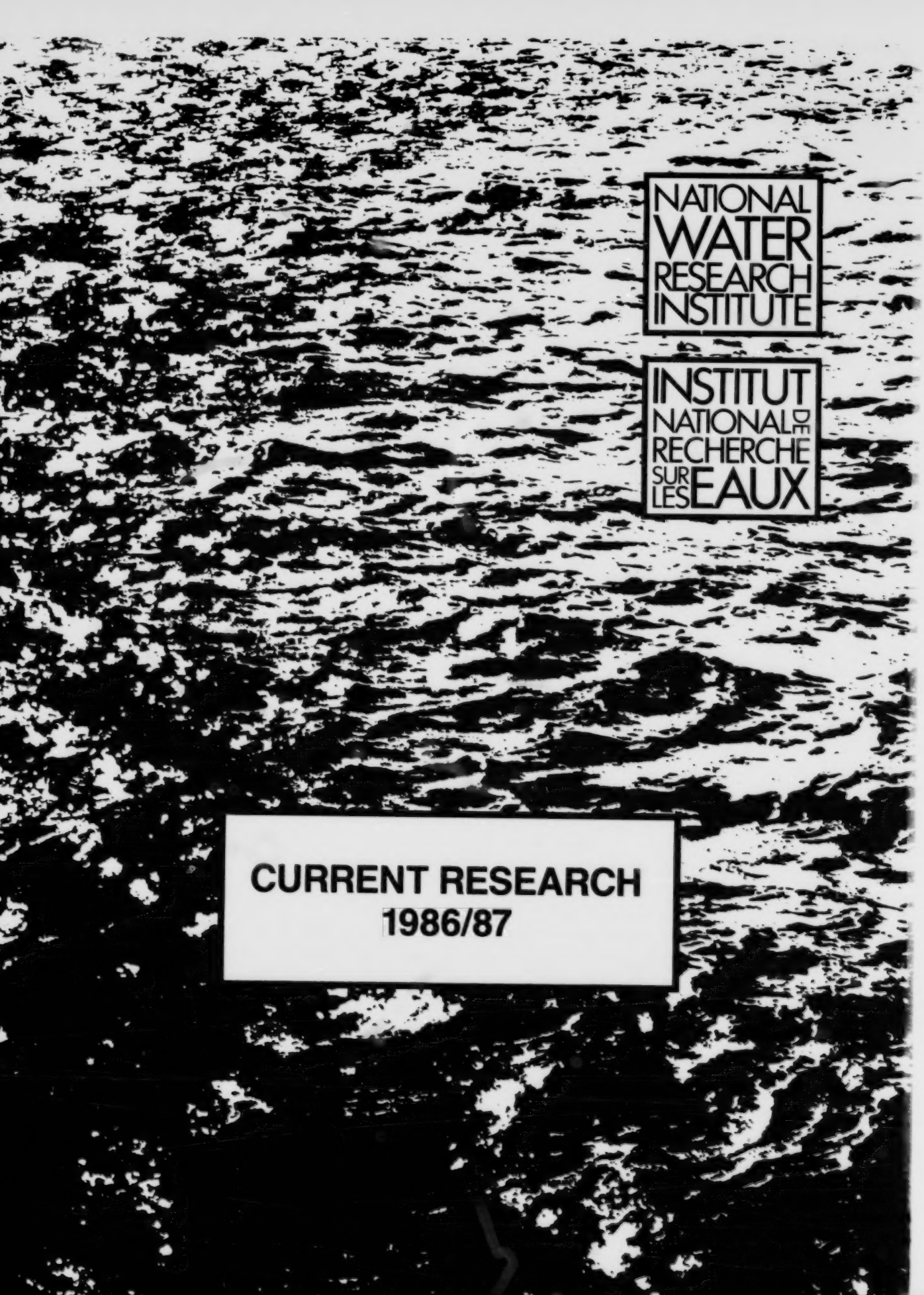

NATIONAL WATER RESEARCH INSTITUTE

INSTITUT NATIONAL DE RECHERCHE SUR LES EAUX

CURRENT RESEARCH 1986/87

CURRENT RESEARCH

1986/87

National Water Research Institute
Inland Waters/Lands Directorate
Burlington, Ontario
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Environment Canada | Environnement Canada

Conservation and Protection | Conservation et Protection

D.L. Egar

It is with great pleasure that I introduce CURRENT RESEARCH 1986/87, the annual science report of the National Water Research Institute (NWRI). I hope it will provide the water research community with a useful overview of our progress in the past year.

NWRI is the largest freshwater research institute in Canada and plays a lead role in developing the scientific expertise and knowledge required by Environment Canada to understand and resolve water issues of national significance. To achieve its goals, NWRI conducts a multidisciplinary program of targeted basic research, applied research, and experimental development concerned with the full range of freshwater problems facing Canada. Through the expertise of the scientists, the Institute advises Environment Canada on priority issues, provides leadership on rapidly developing or emerging water science programs, represents the Department in national and international water science organizations, and serves in a public spokesperson role on the science dimensions of Canadian water issues.

In retrospect, 1986/87 has been a year of change and accomplishment for NWRI, as we restructured our organization and refocused our research. The Institute is now organized into multidisciplinary project groups, each project focusing on advancing our expertise and understanding of a high priority freshwater science issue. The projects, led by senior research scientists, are linked together into three research Branches, supported internally by centralized research support, science liaison, and staff services divisions. The structure is simple and accountability is clear. At the same time, the project groups are flexible, and membership can evolve as the issues evolve.

Taken together, the fourteen projects which currently comprise the Institute's research program address the science needs of many of the important water issues facing Canada over the next decade. In designing the projects, strategic emphasis has been given to investigating critical interactions between environmental compartments which control the fate and effects of pollutants, to understanding the dynamics of critical regional ecosystems, and to developing state-of-the-art aquatic measurement and assessment methodologies.

In this first edition of CURRENT RESEARCH, the scientific staff report on the year's progress in their individual studies. In the Lakes Research Branch the focus is on environmental quality, especially toxic chemicals, and on the chemical, biological and physical factors that influence the fate and effects of pollution in Canada's lakes (sediment-water and nutrient-contaminant interactions, toxic rain, climate change, lake restoration, contamination of the Great Lakes connecting channels). In the Rivers Research Branch, the focus is on land-water interactions occurring in rivers and river basins affected by human activities (pesticide effects, groundwater contamination, acid rain, ecotoxicology, and water quality/quantity modelling and monitoring research). Lastly, in the Research and Applications Branch, the emphasis is on analytical chemistry research and methods development, quality assurance, and hydraulics processes.

These results represent the best efforts of the Institute's talented staff to advance and communicate new knowledge of scientific merit and practical importance. It is my hope that this knowledge, and the commitment to excellence of the staff who produced it, will contribute significantly to the future protection and sustainable development of Canada's freshwater resources.

D.L. Egar
Executive Director
National Water Research Institute

Canada

SYNOPSIS

The research accomplishments of the National Water Research Institute (NWRI), Inland Waters/Lands Directorate, Environment Canada, for the fiscal year 1986/87 are summarized. The Institute, located in Burlington, Ontario, undertakes original research and development on freshwater issues of national significance to Canada.

The research objectives, results and publications of the Institute's professional staff are summarized individually. Studies are reported by project, each of which addresses an important Canadian freshwater science issue. The following fourteen projects, grouped into three research Branches, comprise the NWRII 1986/87 research program: Lakes Restoration, Great Lakes Connecting Channels, Air-Water Interactions, (climate change, "toxic rain"), Nutrient/Contaminant Interactions, Sediment-Water Interactions, Long Range Transport of Airborne Pollutants, Water Quality Monitoring/Modelling, Contaminants/Pesticides, Groundwater Contamination, Water Quantity Modelling/Monitoring, Ecotoxicology, Analytical Chemistry Research, Quality Assurance and Hydraulics Studies.

Le présent document résume les recherches accomplies au cours de l'année financière 1986-1987 par l'Institut national de recherche sur les eaux (INRE) qui fait partie de la Direction générale des eaux intérieures et des terres d'Environnement Canada. L'Institut, situé à Burlington en Ontario, est à la source des programmes de recherche et de développement qui traitent des problèmes de l'eau douce d'importance nationale au Canada.

On présente le résumé de chaque objectif, résultat et publications étant liés aux travaux des chercheurs de l'Institut. Les études sont répertoriées par programmes qui traitent chacun d'un problème scientifique important dans le domaine de l'eau douce au Canada. Les quatorze programmes suivants, qui relèvent de trois directions de recherche distinctes, composent le programme global de recherche 1986-1987 de l'INRE : régénération des lacs, voies d'eau reliant les Grands Lacs, interactions air-eau (changement climatique, pluies toxiques), interactions substances nutritives-contaminants, interactions sédiments-eau, transport à grande distance des pollutants atmosphériques, surveillance et modélisation de la qualité de l'eau, contaminants et pesticides, contamination des eaux souterraines, surveillance et modélisation de la qualité des ressources en eau, écotoxicologie, recherche en chimie analytique, assurance de la qualité et études d'hydraulique.

Lakes Research Branch

R.J. Allan, Director

R.J. Allan

The Lakes Research Branch conducts applied research to provide effective management options to conserve and protect Canada's freshwater lakes. Lakes include all natural lakes as well as man-made impoundments of all sizes throughout Canada. Also included are the few large freshwater upper estuaries of major rivers, particularly the St. Lawrence and Fraser rivers.

Research is conducted into the critical limnological processes and the chemical, biological, and physical factors affecting the rates of these processes, which, in turn, influence the fate and effects of pollutants. Emphasis is on toxic organic chemicals, but also included are toxic metals, radionuclides, nutrients, and traditional parameters such as dissolved oxygen content. The impact of lake trophic state on toxic chemical fate and effects is a major area of interest because of the existing nutrient control programs for lakes and controlled toxic chemicals load (as opposed to concentration) limits. Research emphasis is on quantification of the transfer of materials (toxic chemicals, nutrients, sediments, gases) across interfaces between the three major environmental compartments of the bottom sediments, the water column together with its abiotic particulates and biota, and the atmosphere.

A variety of physical, chemical and biological processes and their rates need to be quantified and modelled for purposes of predicting pollutant fate and effects and lake ecosystem recovery time, and for assessing the impacts and feasibilities of remedial options for polluted aquatic ecosystems. These processes and rates include:

- hydrological cycles of lakes;
- assessment of long-term water quality trends;
- external and internal loadings of pollutants;
- sources, transport and movements of water masses and their associated particulate loads;
- partitioning of pollutants between media in the water column;
- partitioning of pollutants between the water and the atmosphere;
- burial of contaminants in bottom sediments;
- sedimentation versus resuspension rates;
- bioperturbation;
- degradation and bio-uptake of pollutants;
- food chain transfer by benthic organisms of sediment-associated pollutants;
- evaluation of ecosystem health;
- rehabilitation potential of lakes and reservoirs;
- in-lake restoration methods;
- manipulation of aquatic food chains.

Also included are ecotoxicology assessments of pollutant effects, especially of pollutant mixtures, using techniques such as bioassays, and prediction of pollutant effects by techniques such as quantitative structure activity relationships. Comparisons between real and model ecosystem impacts is an important aspect of this activity. Possible means of *in situ* restoration of polluted or degraded lakes and impoundments are also investigated as are the effects of induced or controlled biomanipulation of food webs.

PUBLICATIONS

Allan, R.J. 1986. The limnological units of the Lower Great Lakes - St. Lawrence River Corridor and their role in the source and aquatic fate of toxic contaminants. Water Poll. Res. J. Can. 21(2): 168-186.

Allan, R.J. 1986. The role of particulate matter in the fate of contaminants in aquatic ecosystems. IWD SS 142, 128.

Allan, R.J. 1987. Relevance of contaminated sediment studies in the Great Lakes to pollution assessment and control in the Mediterranean Sea. Water Sc. & Technol. 18(9): 317-325.

Great Lakes Areas of Concern: Ecosystem Stability

J.M. Barica, Study Leader

J.M. Barica

INTRODUCTION

This study was established in the latter part of 1986 with the following objectives:

1. To gather available information on the IJC Areas of Concern in Canada, to follow up on the development and implementation of Remedial Action Plans (RAPs); to coordinate LRB's input; and to collate information on the Great Lakes recovery trends.

2. To carry out limnological research in selected Areas of Concern to supplement RAP research needs, particularly in (i) analyzing causes and consequences of nitrate increases in the Great Lakes, and (ii) assessing impacts of ammonia contamination of Hamilton Harbour (with LRB Lakes Restoration Project team).

3. To provide liaison with Canadian and foreign universities and aquatic research organizations.

RESEARCH RESULTS

Compilation of available information on the Canadian Areas of Concern was initiated with LRB's input into the RAP process recorded and coordinated with RDG's requirements. Particular reference was given to Hamilton Harbour and Severn Bay, and literature survey conducted. Field measurements of ammonia contamination in Hamilton Harbour together with collection of other limnological parameters started in February, with high frequency sampling periods (daily for four weeks, later weekly), and corresponding flow measurements in the ship canal. Samples for bacteria, protozoan, phytoplankton and zooplankton identifications were also collected.

Literature survey for nitrate increases in Great Lakes and other water bodies in Canada and abroad was initiated and division of responsibilities in data interpretation with collaborating agencies was established. A computer program was developed to enable computation of nutrient dissolved oxygen and phytoplankton biomass oscillations for assessment of ecological stability, and applied to data from several disturbed lakes in Western Canada. Extensive summaries and reviews of previous work on hypereutrophic lakes were prepared and submitted for publication.

An inventory of NWRI linkages with Canadian, U.S. and overseas universities was prepared and analyzed. Closer ties were established with McMaster and Waterloo universities. Cooperative projects were proposed and designed with University of Alberta, the Technical University of West Berlin, University of Konstanz, West Germany, and Chiang Mai University in Thailand (CIDA funding, proposal with R.J. Allan). Invited lectures were presented at Charles University in Prague, Czechoslovakia, and the Czechoslovak Academy of Sciences. A special workshop, requested by IJC and IW/LD-OR, was convened to analyze the utility of soluble reactive phosphorus measurements in Great Lakes surveillance programs and a report with recommendations was prepared.

PUBLICATIONS

Barica, J. 1986. Cyclic ecological instabilities in hypereutrophic lakes of Western Canada. Synopsis, Selected Papers on Hypereutrophic Lakes, 34 pp.

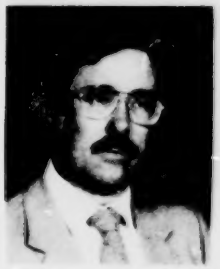
Barica, J. 1987. Water quality problems associated with high productivity of Prairie lakes in Canada: A review. *Water Quality Bulletin.* 12(3): 107-129. In press.

Barica, J. Research on eutrophication and its applicability to fish farming in third world countries. Proc. of a workshop, University of Western Ontario. In press.

Barica, J. and Allan, R.J. 1987. An analysis of the utility of SRP measurements in Great Lakes surveillance programs. NWRI Contribution 87-73.

Lakes Restoration

M.N. Charlton, Project Chief



M.N. Charlton

The Lakes Restoration Project conducts research on the means and progress of damaged lake restoration. All of the Laurentian Great Lakes have been damaged by pollution in the past. Presently, the Canada/U.S. Great Lakes Water Quality Agreement limits the amount of pollution. Since controls began in the early 1970s, there has been a gradual response as loadings have been reduced to targeted levels. Some aspects of water quality, however, have not responded as predicted and these require further research on how to detect changes, how to measure loadings, and whether further controls or treatments are needed. The problems of the Great Lakes also occur across the country in smaller lakes fed by agricultural and urban sources.

Environmental measurements in the Great Lakes are difficult to interpret due to variations caused by weather and the limitations of sampling programs. The Great Lakes Surveillance Project includes original statistical research and pollution loadings. Contributions to IJC committees on surveillance are coordinated and other scientific inputs to the surveillance program are organized. The trends in abundance of nuisance algae, *Cladophora*, are followed and the reasons for the long-term trend in nitrate in the Great Lakes are studied. Shoreline erosion processes are studied and a data base on sediment properties of the Great Lakes is maintained.

Hamilton Harbour is one of the most polluted bodies of water in North America. As such, it is listed as an Area of Concern by the International Joint Commission and work has begun on a Remedial Action Plan (RAP). The Lake Restoration Project conducts research on methods to test and evaluate schemes to re-oxygenate the bottom waters of the harbor, which are rendered anoxic by pollution. The depth of contaminated sediment deposits is being charted and the redistribution of the contamination due to dredging and natural currents is investigated with sediment traps. Experiments are conducted on sediment properties and the possibility of sealing contamination into the sediments with the addition of locally available lime.

The invasion of some inland waterways by exotic water weeds has rendered them almost useless for recreation. Recent disappearances of the weeds seem connected to large numbers of insect larvae. This is being investigated to determine the feasibility of biological control. Other factors, such as turbidity, water levels, and the presence of carp, inhibit weeds necessary for fish production. These are being investigated to find ways to re-establish valuable species of weeds. Weeds are also being used to measure the biological availability of contaminants in sediments which may be dredged. Research will show the best species of plant to use and the environmental impact of uptake of contaminants by plants.

Lakes Restoration activities provide expertise and scientific investigation for lake restoration anywhere in Canada. Work includes experiments on dredging small lakes, adding oxygen and applying lime as ways of ameliorating water quality problems due to natural and human causes. Sediment feedback of phosphorus may retard cleanup effects of phosphorus load reductions. This is studied as a contribution to the Bay of Quinte RAP.

Hamilton Harbour Rehabilitation Oxygen and Sedimentation Regime

M.N. Charlton, Study Leader

T.P. Murphy
J.S. Ford

INTRODUCTION

The oxygen regime in Hamilton Harbour is characterized by early stratification and rapid deoxygenation of the bottom waters. This is thought to be caused by excessive algae growths which settle to the bottom, thus providing the organic matter which consumes oxygen. The settling algae plus other sediment sources result in the binding of contaminants and their subsequent burial in the harbor bottom. These related processes present the problems of methods to test and document remedial oxygenation schemes and whether contaminant deposits stored in sediments are resuspended into the water column.

RESEARCH RESULTS

The NWRI Water Quality Profiler designed for Lake Erie was further developed with the addition of pH, turbidity, and conductivity to the existing oxygen, temperature and depth sensors. The profiler was used to measure the variation of oxygen with depth at many stations. This was done to find the effect of oxygen injection apparatus (see report by T. Murphy in this section). Profiles in the region of the oxygen injector showed elevated oxygen concentrations as hoped. The full suite of oxygen, temperature, depth, pH, conductivity, and turbidity sensors were demonstrated on several occasions. Near the entrance and exit of the harbor, the profiler showed the interaction of Lake Ontario water with Hamilton Harbour water. Figure 1 shows profiles from a station near the Burlington Canal outlet. Water from Lake Ontario has a lower temperature, less conductivity and more oxygen than does Hamilton Harbour water. The oxygen problem in the harbor is shown by the zero readings in Figure 1, while the intrusion of higher quality lakewater is shown in the mid-depth area of the profiles. These intrusions of lakewater help to ameliorate oxygen depletion. This test showed that the profiling apparatus is able to track and determine the extent of influence of larger oxygenation schemes in upcoming experiments. Transect profiles (Fig. 2) across the harbor showed that fall mixing proceeds more rapidly in the shallower water. The slightly elevated oxygen levels there indicate that horizontal mixing is not necessarily extreme.

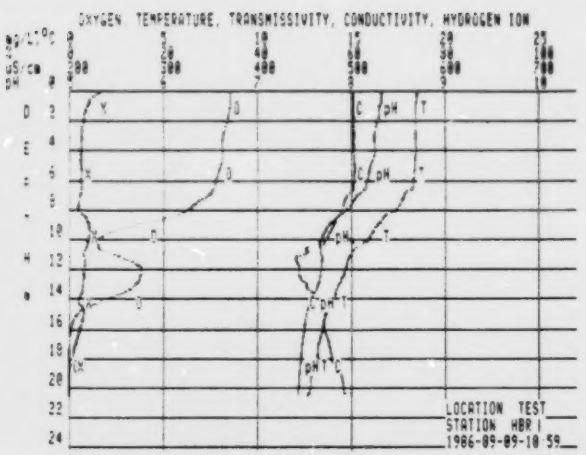


Figure 1. Profiles of oxygen, temperature, conductivity, pH and turbidity (x) in Hamilton Harbour recorded with NWRI Water Quality Profiler.

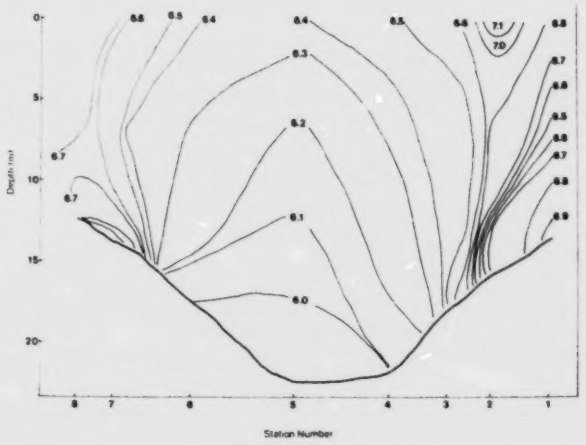


Figure 2. Isoplets of oxygen across Hamilton Harbour showing delayed horizontal mixing of oxygenated water nearshore.

Sediment traps showed that the basic rate of downflux is about five times as high as in Lake Ontario (Fig. 3. In addition, traps at 22 m caught more material than traps at 15 m. This means there is resuspension of bottom sediments, as has been found in other areas of the Great Lakes.

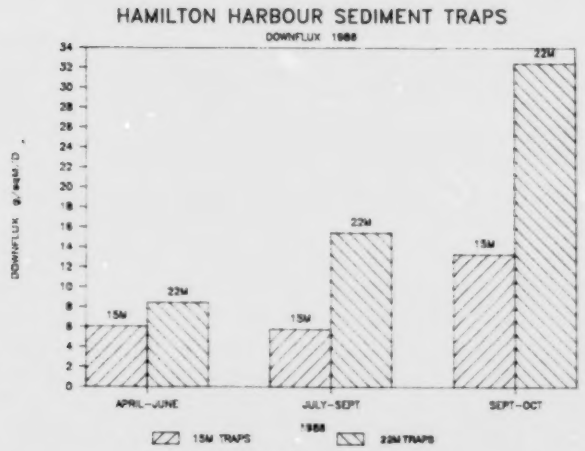


Figure 3. High sediment trap catch rates in Hamilton Harbour show resuspension of bottom sediments.

PUBLICATIONS

Desrosiers, R., Pedrosa, M. and Savile, H. 1987. Sealing reliability of three adhesives for acrylic to aluminum bonding under cyclic pressure and temperature loading. RSD/ESS Tech. Note 87-04.

Availability of Heavy Metals and Phosphorus in Suspended and Bottom Sediments of the Detroit River and Hamilton Harbour

P.G. Manning, Study Leader

T. Mayer

P.G. Manning

INTRODUCTION

Iron compounds play an important role in the availability of phosphate and heavy metals in aquatic ecosystems. Under oxic conditions, iron compounds (e.g., Fe^{3+} oxides) remove and retain phosphate and heavy metals from the water column by adsorption and/or precipitation. The principal iron compounds can be measured quantitatively by computer deconvolution of the Mossbauer spectra.

The Mossbauer spectra of suspended sediments from the Detroit River and Lake St. Clair are simple and are similar to those of unpolluted sediments, indicating the presence of ferrous ions in chlorite and ferric ions in mainly hydrated ferric oxides and clays. The non-apatite inorganic phosphorus (NAIP), which is probably the main source of bioavailable P, is generally associated with the ferric ion from the ferric oxides.

The Mossbauer spectra of suspended and bottom sediments of Hamilton Harbour, however, are much more complicated. In addition to commonly occurring natural iron compounds, the spectra reveal the presence of iron forms originating from the steel industry. The concentrations of each iron compound can be correlated to the concentration of heavy metals and phosphorus and used as an indicator of contaminant transport and deposition in the harbor.

The main objective of the Detroit River study is to determine if iron, phosphorus and lead interactions in the Detroit River are different from those in Lake St. Clair due to the input from major cities and industries located on the shores of the Detroit River.

The main objective of the Hamilton Harbour study is to determine the concentrations of forms of iron from anthropogenic activities, heavy metals and phosphorus in suspended and bottom sediments in order to assess the importance of municipal and industrial point sources and evaluate the fate and transport of anthropogenic material within the harbor.

RESEARCH RESULTS

Detroit River

The Mossbauer spectra of suspended solids from the Detroit River and Lake St. Clair are simple and comprise the doublets of ferrous ions in chlorite and ferric ions in mainly hydrated ferric oxides and clays. The Fe^{3+}:Fe^{2+} ratios are typically in the range of unpolluted sediments, and the spectra show no obvious peaks corresponding to man-made wustite and hematite (e.g., as observed in Hamilton Harbour).

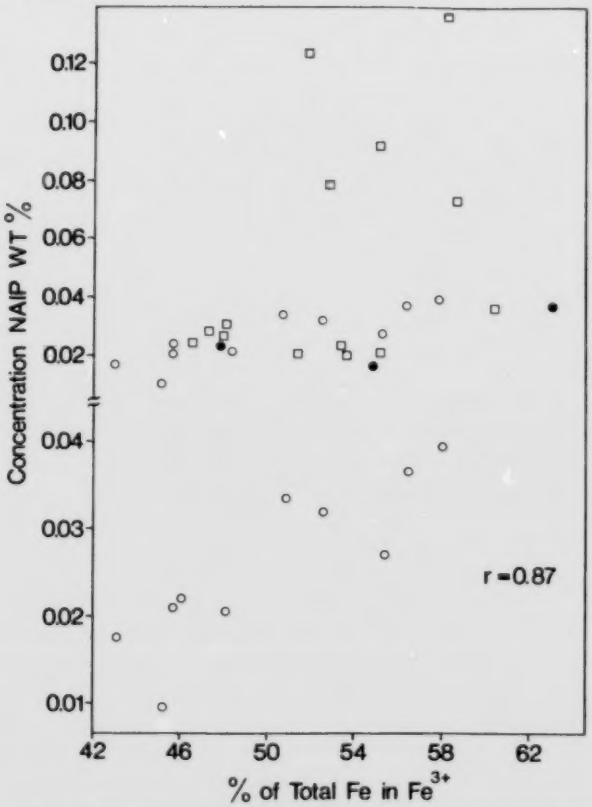


Figure 4. Plots of concentrations of NAIP against Fe^{3+} for Lake St. Clair sediments 1985 cruise (•), Lake St. Clair 1986 (•) and Detroit River (□). Note the five outliers (□).

Concentrations of NAIP and Fe^{3+} (as % of total iron) are well correlated for the suspended solids of Lake St. Clair ($r=0.87$) (Fig. 4). If most of the Detroit River data are included, the correlation is less good ($r=0.60$) (Fig. 4). The five outliers mark stations on the west side of the Detroit River and indicate sources of phosphorus with minor input of ferric iron. This excess of NAIP is probably highly bioavailable. Fe^{3+}-NAIP correlations suggest that nutrient properties on the east side of the Detroit River are similar to those of Lake St. Clair.

Concentrations of Pb and Fe^{3+} are poorly correlated for the Lake St. Clair solids ($r=0.30$) (Fig. 5). The paucity of points, however, suggests that no correlation exists. If the Detroit River data are included, excluding the four outliers marking the same west-side stations as in Figure 4, then $r=0.2$, i.e., no correlation exists. No significant sources of lead occur on the east side of the Detroit River.

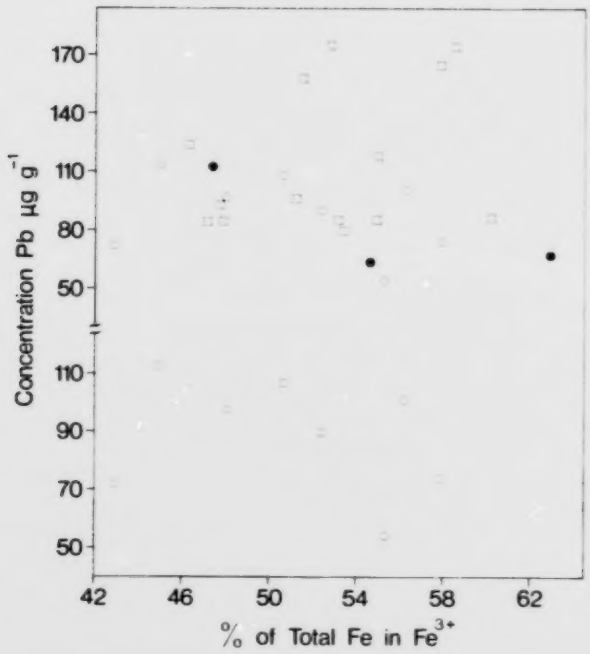


Figure 5. Plots of lead concentrations against Fe^{3+} for Lake St. Clair 1985 (◦), Lake St. Clair 1986 (•) and Detroit River 1986 (□).

Hamilton Harbour

Deconvolution of the Mossbauer spectra (Fig. 6) reveals the presence of Fe^{2+} in chlorite (natural origin), ferric ions in clays and amorphous hydrated oxides (natural and anthropogenic), haematite (α-Fe_2O_3) (anthropogenic) and wustite ($Fe_{1-x}O$) (anthropogenic). Computed areas beneath the peaks are proportional to the abundance of the iron compound (Fig. 6); 14% of total iron is Fe^{2+}, 44% is Fe^{3+}, 28% is in haematite and 14% is in wustite. Chlorite, haematite, and wustite, being detrital and crystalline, play a minor role in binding metal and phosphate ions. All four compounds were measured at all stations, including those near inflows from Coote's Paradise and the Windermere Basin. Preliminary interpretation suggested that a surface plume rich in Fe, Pb and Zn emanates from the Stelco-Dofasco complex in the southeastern end of the harbor.

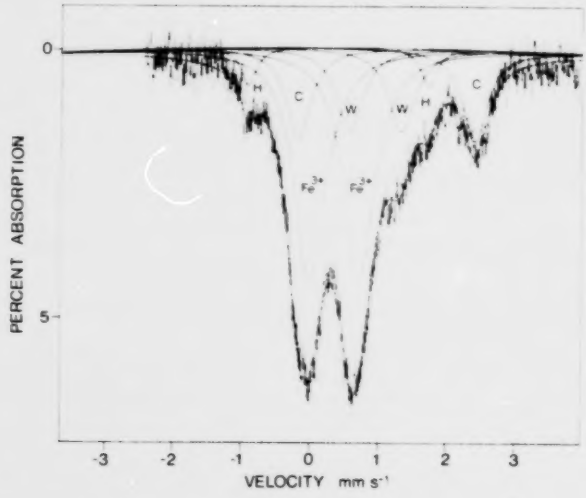


Figure 6. Resolved component doublet in Mossbauer spectra of Hamilton Harbour suspended sediment. C=Fe^{2+} in chlorite, H = haematite, W = wustite, and Fe^{3+} = ferric iions in clays and amaorphous oxides.

Concentrations of Pb and Zn are well-correlated with concentrations of total Fe, haematite and wustite in the suspended particulates. In contrast, Cd, Ni and P are not well-correlated with total Fe. At all stations, Fe^{3+}:Fe^{2+} ratios are higher for the suspended particulates than for bottom sediments at the sediment-water interface. Because Fe^{2+} in chlorite can be considered a conservative element, then significant amounts of Fe^{3+} may be regenerated at the sediment-water interface. That would allow regeneration of heavy metals associated with Fe^{3+} oxides.

The impact of P-loading from municipal point sources is apparent from higher than average values of NAIP concentrations in suspended solids from location adjacent to the entrance to the Windermere Basin and from the vicinity of the Burlington sewage treatment plant.

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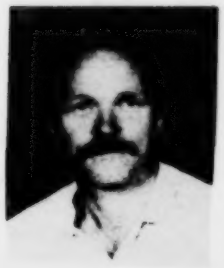
Lake Restoration in Hamilton Harbour and Small Lakes

T.P. Murphy, Study Leader

M.N. Charlton
W. Booth
P.G. Manning
T. Mayer



T.P. Murphy

INTRODUCTION

Although all lake managers agree that treatment of the source of contaminants is the most important step in a remedial action plan, the rehabilitation of naturally eutrophic lakes or the restoration of badly contaminated sites such as Hamilton Harbour requires direct treatment. Our project has been studying methods to improve water quality of the harbor. This research was complemented by whole-lake treatment of naturally eutrophic lakes in western Canada. The work at Black Lake, British Columbia, is complete and has influenced the work on lime treatment of Alberta lakes. The aim of the Alberta study is to develop an inexpensive, nontoxic, technique for the control of excessive algal growth. The product should be better recreation, improved fisheries, and nontoxic drinking water supplies.

RESEARCH RESULTS

Hamilton Harbour

Three methods of oxidizing the hypolimnion of Hamilton Harbour have been evaluated:

1. Hypolimnetic aeration (with air) is the cheapest to operate, but the capital cost is high ($4-40 million). Shore-based units could be installed to minimize interference with shipping.

2. Oxygen injection (with pure oxygen) with diffusers would cost about a tenth of the cost of hypolimnetic aeration to install. Diffusers would be a threat to shipping in some locations and destratification may restrict growth of cold-water fish. Oxygen injection by diffusers has an advantage that if reductions in oxygen demand occur (i.e., by improved sewage treatment), the oxygen injection system can be easily adjusted without decommissioning expensive equipment.

3. Oxygen injection with equilibration tanks (with pure oxygen) could be done with shore-based units. This method would maintain stratification, but it could be the most expensive method of increasing the oxygen concentration.

Pilot Scale Oxygen Injection

On October 4, 1986, NWRI installed an oxygen storage tank on the City of Hamilton's future harbor park with Linde Ltd., and a 760 m pipe on the bottom of the harbor to connect the oxygen tank with a large diffuser. About half of the oxygen dissolved. The oxygen injection did not result in any sediment resuspension into the harbor. No complaints of smell, noise, or navigation disruptions were received. This experiment increased the oxygen content of only a small part of the harbor. Several problems were resolved and we are confident that this technique could be used to improve the western portion of the harbor by using six to ten times as much oxygen as our pilot test.

Treatment of just the western basin could provide suitable habitat for recreational fishing. Moreover, some organic contaminants would decay faster by increasing the oxygen concentrations.

Several experiments on the effects of oxygen treatment were done in the NWRI laboratory with model enclosures containing harbor water and sediment from two harbor sites. In the water column, oxygen injection reduces bacterial activity. Oxygen injection increased the clarity of microcosms of Hamilton Harbour by inducing the precipitation of the following proportion of the metals: copper (49%), iron (45%), lead (40%), manganese (35%), and zinc (78%).

Lime Treatment

In laboratory enclosures of harbor water and sediment from three sites, lime precipitated the following proportion of metals: chromium (23%), copper (61%), iron (52%),

manganese (40%), lead (51%), and zinc (20%). A precipitation of metal contaminants should improve the growth of microorganisms (and fish) and reduce the effect of the harbor on Lake Ontario. The Hamilton Harbour Commission allowed a preliminary experimental use of lime in a pond neighboring the bird colonies on the future East-Port property. Canadian Wildlife Service officers observed no adverse effect on wildlife. Unlike in NWRI experiments in Alberta or British Columbia, an algal bloom persisted; chemicals in the lagoons may have interfered with calcite precipitation.

Remedial Action Plan

NWRI was very active in the remedial action plan process. As well as our research to determine the cost-benefit of restoration programs, sections of the Remedial Action Plan were written on phytoplankton, zooplankton, sediments, techniques available for direct treatment, oxygen, and ammonia. NWRI staff were present at each stakeholder meeting as technical resource experts. The Hamilton Harbour Study was presented in several public meetings and in many meetings with government agencies, industrial and consulting firms. The study was reviewed by radio, TV, newspapers and magazines.

Figure Eight Lake, Peace River District, Alberta

Figure Eight Lake is highly productive and subject to periodic winterkill. This condition has hampered the establishment of a recreational fishery on the lake. The purpose of our investigation was to evaluate why current management practices were unsuccessful and what would be the most efficient and economical way to enhance the water quality and thus the recreational fishery. Because Figure Eight Lake is similar to many shallow productive lakes on the Canadian prairies, a successful treatment of Figure Eight Lake could be applied to many other prairie lakes.

Analysis of Earlier Treatments

Figure Eight Lake received a total of 372 kg of the algicide copper sulfate (1980, 1983 and 1984). Although the application doses were typical of most treatments in Canada (19–71 μg/L) concern over the long-term effects was expressed when the amphipod population drastically decreased and when oligochaetes and chironomids were common only deep in the sediment (greater than 8 cm).

Analysis of sediment cores indicated that the copper sulfate treatments greatly changed the sediment and water biogeochemistry. The organic carbon content of the sediment was reduced by 50%. Mossbauer spectrophotometry and chemical extractions indicated that pyrite formation was blocked. Data collected before and after the copper sulfate treatments indicated that the sulfate concentrations in the lake water had tripled. Apparently, the sulfate-reducing bacteria in the sediments had been suppressed.

This hypothesis was confirmed by heterotrophic analysis. The rate of acetate assimilation in the Figure Eight Lake sediments was minimal where the copper concentration was highest 2–4 cm below the surface. The rate of acetate assimilation was much higher in sediments from an untreated lake (Amisk Lake near Boyle) and the depth profile of acetate assimilation was quite different.

Although the copper treatment had reduced the production of algae and fish food, copper treatment did not result in good water quality. Intense algal blooms redeveloped weeks after the copper sulfate treatment. Moreover, the high summer productivity resulted in rapid winter oxygen depletion which resulted in fish kills.

Lime Treatment

Figure Eight Lake was treated with calcium carbonate and calcium hydroxide. The calcium carbonate treatment successfully reduced algal biomass from 300 μg/L to 5 μg/L, and increased the water transparency 20-fold. The effects of the $CaCO_3$ lasted 5 weeks. The $Ca(OH)_2$ treatment was not as effective. The lime treatments had no adverse effects on fish or their invertebrate food. Simple conclusions were restricted by a concurrent study that indicated that Figure Eight Lake may not have been a good lake to treat with lime. A study of iron geochemistry indicated that Figure Eight Lake is unusually rich in iron. Lime precipitates phosphorus in carbonate-rich lakes, but some studies indicate that lime should dissolve sediment phosphorus in iron-rich lakes.

Chain Lake, British Columbia: Study of a Water Diversion and Sediment Phosphorus Release.

In 1968, a 2-km long water diversion was built to flush Chain Lake, British Columbia, with nutrient-poor subalpine water. Unfortunately, in some years, blue-green algal blooms (chl *a* greater than 100 μg/L) and fish kills still occur. The incomplete success of the diversion is related to the asynchrony of water flow and phosphorus release from the sediments. Internal loading represents about 78% of the phosphorus supply to the lake in summer, and water flow is minimal during phosphorus release. Phosphorus is five times more concentrated in the surface sediments relative to sediments deeper than 80 cm. Diatoms in sediment cores indicate that the lake has been eutrophic for at least 300 years. The accumulation of a diatomaceous ooze in the lake was measured by three methods to be between

0.5 and 1 cm a year. A larger diversion would suppress plankton blooms, but in this shallow lake it would enhance the growth of macrophytes; sediment dredging may be a more effective *in situ* treatment. A consulting firm has proposed a dredging experiment in Chain Lake based on this recommendation.

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Causes of Aquatic Plant Decline in the Ontario Lakes

D.S. Painter

D.S. Painter

INTRODUCTION

Milfoil Decline in the Kawartha Lakes

Eurasian watermilfoil is an aquatic plant causing serious impairment of the recreational potential of many areas in Ontario, Quebec and British Columbia. Eurasian watermilfoil invaded the Kawartha Lakes area of Ontario in the late 1960s. Milfoil has, however, been observed to decline in lakes after infesting the lake for several years. Rapid disappearances of milfoil were observed in Chemung Lake and Rondeau Bay in 1977. No explanation for the disappearances was apparent. Similar disappearances of milfoil were observed in the 1970s in Lake Wingra, Wisconsin, and in the 1960s in Chesapeake Bay, Maryland. Studies of the disappearance phenomena in the U.S., conducted after the fact, examined pesticides, pathogens, diseases, sediment nutrition, sediment density, water chemistry, climate, toxin accumulation, epiphytic and macrophytic competition. The conclusion was that no one factor could be identified as responsible.

We are attempting to isolate the cause(s) of the natural decline. Since 1977, we have observed a slow decline of milfoil from Buckhorn Lake (Figures 7, 8); and since 1980, we have attempted to determine if the sediments are responsible. Recent research results from projects conducted by the U.S. Army Corp of Engineers and ourselves indicate that increased organic content of the sediments as a result of milfoil litter accumulation is responsible for decreased growth rates of milfoil due to sediment nutrient dilution. Therefore, this project sampled several locations in the Trent-Severn-Rideau waterway where milfoil was still present and where milfoil had recently disappeared. Sediments were collected at approximately 15 locations, and growth experiments were conducted to determine if the sediments could support milfoil growth. Growth rates of milfoil on the "good" and "bad" sediments were compared to determine if the sediments were responsible for the disappearance of the milfoil from the stations sampled.

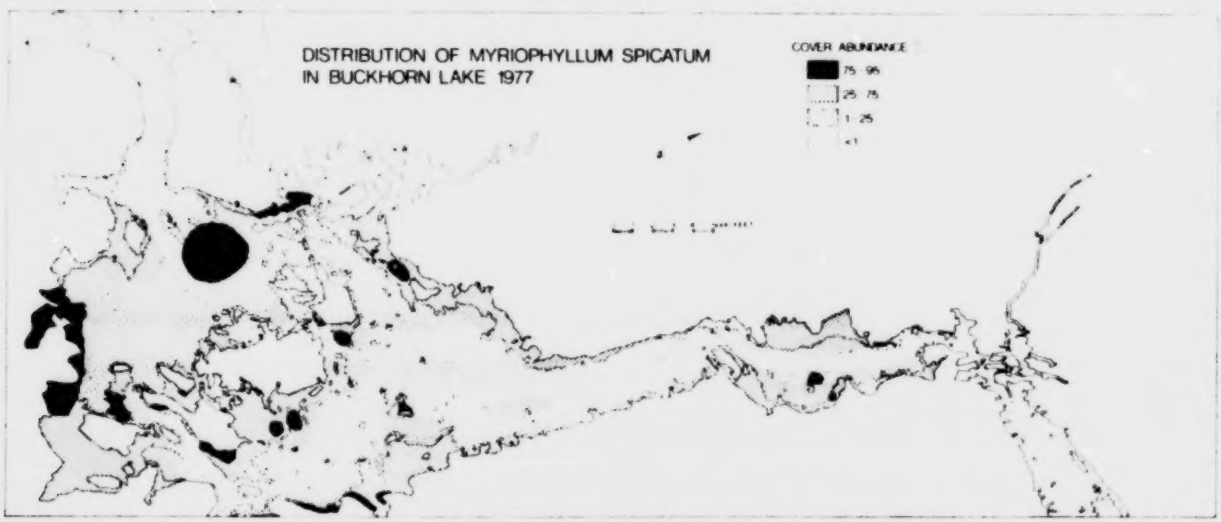

Figure 7. Aquatic vegetation and milfoil distribution in Buckhorn Lake in 1977.

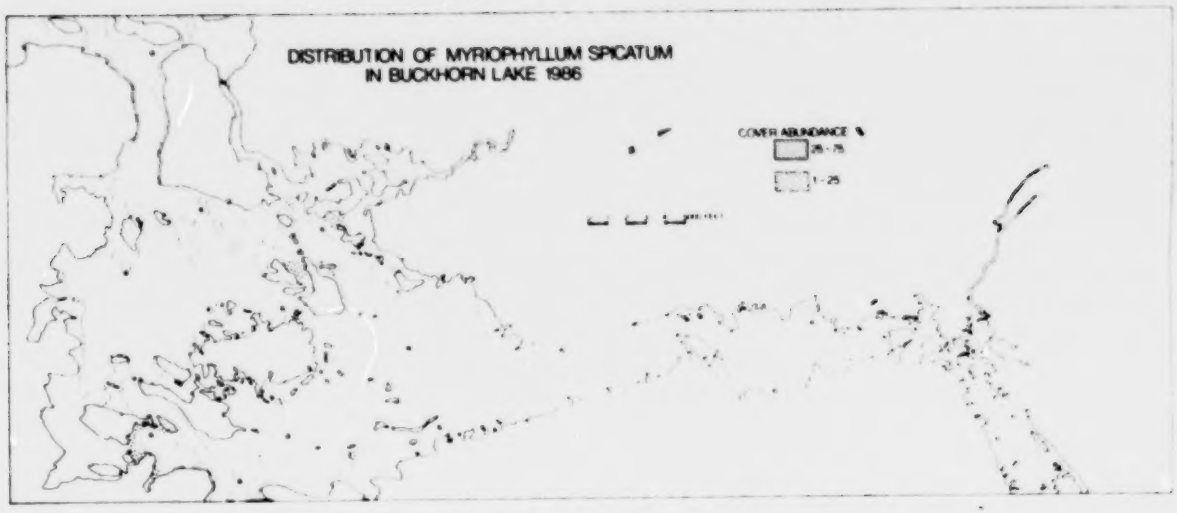

Figure 8. Aquatic vegetation and milfoil distribution in Buckhorn Lake in 1986.

In 1986, a rapid disappearance of milfoil from Scugog Lake was observed and insect grazing was a possible factor. We expanded our program, therefore, to include sediments from approximately 50 locations in four lakes and surveyed 75 sites in 15 lakes for insect grazing damage.

Hamilton Harbour Macrophyte Re-establishment

Macrophyte beds have been identified as a necessary precursor to warm water fishery success in Hamilton Harbour. Available nursery and spawning areas have been dramatically reduced since 1946. The purpose of the study is to identify the factors which may be responsible for the decline of aquatic vegetation in Cootes Paradise and recommend remedial measures.

RESEARCH RESULTS

Milfoil Decline in the Kawartha Lakes

Sediment pore water from three sites where milfoil was absent in one lake was characterized by high ammonia, hydrogen sulfide and low iron, phosphorus and redox potential. Growth experiments ruled out iron limitation and hydrogen sulphide toxicity. Ammonia toxicity was also ruled out. No correlation between milfoil abundance and sediment pore water chemistry, sediment redox potential, sediment geochemistry and milfoil tissue chemistry was observed from 49 sites in four lakes. In growth experiments, a 6.8% reduction in sediment density did reduce growth 42%; but the addition of organic matter in the form of sawdust inhibited growth 81% even though sediment density was not reduced. Some phenolic substances, common in milfoil litter, were toxic, but the concentrations required to illicit a response were high. No significant difference in milfoil growth was evident between "good" and "bad" sites, nor did the addition of nutrients affect the growth rates, thus suggesting that the sediments were not responsible for the rapid decline of milfoil from the Kawartha Lakes.

Insect grazing damage was extensive in the Kawartha and Rideau lakes, and strong circumstantial evidence would suggest that insect grazing was responsible for the disappearance.

The insect believed to be responsible for the grazing damage is an aquatic moth larva *(Acentria nivea)*. The populations of moth larvae were approximately six times greater than previously observed in lakes in the U.S. Previous studies in the U.S. concluded that an individual larva can cause considerable damage, but it remained to be determined whether populations occuring in the field are high enough to measurably reduce milfoil levels.

Hamilton Harbour Macrophyte Re-establishment

The factors being explored are water quality (predominantly clarity), water levels, and carp. Water levels have been responsible for the loss of vegetation acreage, but suitable water levels have existed for the past seven years in Cootes Paradise (Fig. 9) and no response from the vegetation has occurred. A hypsometric curve of Cootes Paradise was generated using soundings collected in 1986 and 1946. The current open-water area is 246 ha with a mean depth of 80 cm. Under normal Lake Ontario water levels, the mean depth would be 70 cm. Comparing the soundings in 1946 to 1986, the western half of the marsh, shallower than 50 cm, has had no net accumulation of sediment; but the eastern half of the marsh, deeper than 50 cm, has experienced a sedimentation rate of 1 cm per

year. Emergent plants in the marsh in 1986 are incapable of colonizing areas of the marsh with depths deeper than 25 cm because they experience flooding damage for too long at depths deeper than 25 cm. The available area for colonization by emergent plants, from the hypsometric information, is less than 5% of the total area.

Water chemistry and water clarity data have been compiled and further sources of information on suspended solids loadings into Cootes Paradise are being explored. Based on the compiled historical water chemistry information, a sampling program has been implemented in 1987. The predominant cause of vegetation loss in Cootes Paradise would appear to be lack of suitable water clarity and littoral area. Water clarity appears to be a function of inputs and resuspension of silt in the shallow western end of Cootes Paradise. Current water clarity measurements (1986), using secchi disc transparency, indicate that the secchi disc transparency was 16 cm. Given the hypsometric curve, less than 2% of the surface area would be available for colonization by submerged aquatic plants. The annual fluctuation of Lake Ontario water levels is 50 cm, with maximums in June and minimums in December. Submerged aquatic vegetation is not capable of colonizing areas of the marsh deeper than 50 cm due to poor water clarity. Water clarity would have to improve significantly (secchi depths greater than 75 cm) before submergent aquatic vegetation would be possible in Cootes Paradise.

Carp exclosure experiments have been attempted, but in the initial experiment, the high water levels in Lake Ontario in 1986 resulted in failure of the exclosure. The site has been moved and appears to be successful to date. Mercer's Glen was chosen for the Carp "exclosure" experiment. The outflow of Mercer's was modified so that water level control was possible. The water level was lowered in the fall and winter of 1986/87, and the Carp in the area were killed. Approximately 150 dead Carp were found in the spring. Literature suggests that 300–400 kg of Carp per ha are sufficient to destroy aquatic vegetation. Given the average weight of an adult Carp is 10 kg, that translates into 30–40 Carp per ha. Mercer's Glen is approximately 2 ha and therefore had 75 Carp per ha. It is, therefore, not surprising that Mercer's Glen did not have any vegetation. Now that the Carp have been eliminated, the submergent vegetation should return.

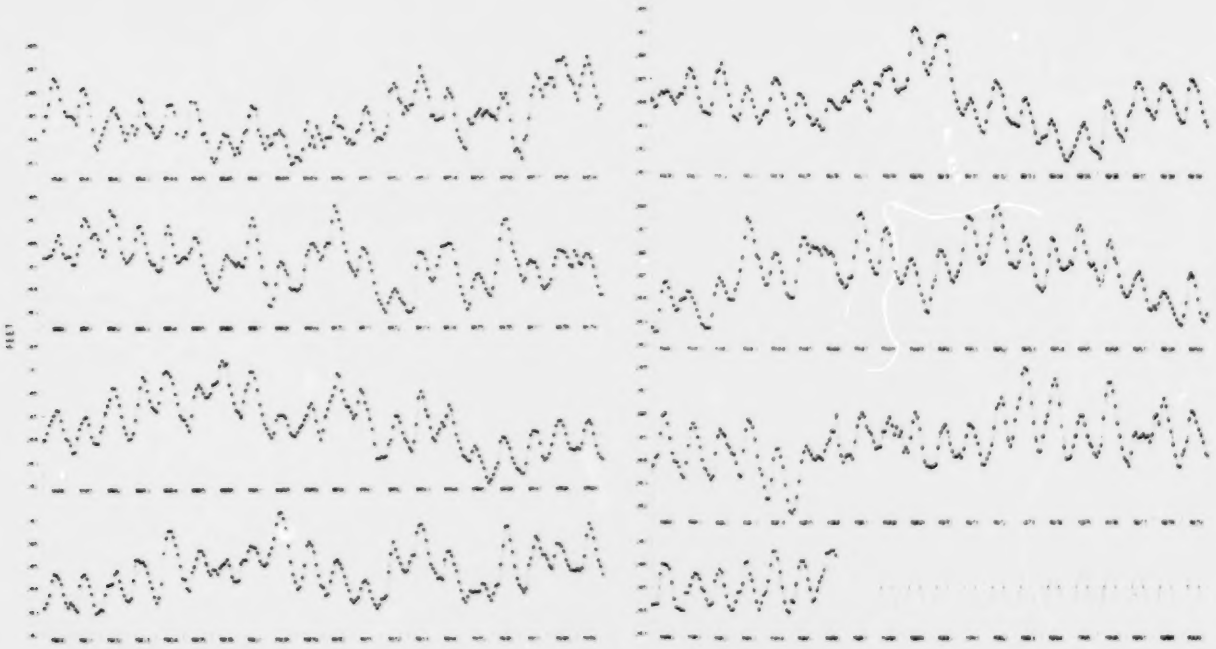

Figure 9. Historical water levels in Lake Ontario.

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Sedimentology of Contaminated Sediments in the Great Lakes and St. Lawrence River

N.A. Rukavina, Study Leader

N.A. Rukavina

INTRODUCTION

The development of models of the transport and accumulation of polluted sediments in the Great Lakes and the St. Lawrence River depends upon information on sediment type, grain size, thickness and stability. This study is concerned with mapping the distribution and thickness of contaminated sediments in several critical areas, and with improving acoustic techniques for measuring thickness and monitoring sediment transport. Sounding and coring surveys have been completed for the Upper St. Clair River, Lake St. Clair, the St. Lawrence lakes - St-Louis and St-Pierre, and acoustic-equipment trials have been conducted in the Hydraulics Laboratory and in Lake St. Clair. Work in 1987–88 will include interpretation of survey data, a sediment survey of Hamilton Harbour, and continued laboratory and field testing of acoustic equipment and procedures.

RESEARCH RESULTS

St. Clair River

The river bed is cut in hard, stoney glacial clay (the Black Shale Till) in mid-channel and in finer glacial silt-clay (the St. Joseph Till) in its upper banks. Sounding records and diver and TV observations indicate that the tills and their erosion products form much of the bed material in mid-channel and that the steep upper slopes are composed of cohesive glacial clay with a thin veneer of unconsolidated sediment, primarily sand and gravel.

Figure 10 shows the thickness of unconsolidated sediment in cores collected along the Canadian shore. Values range from 0 to more than 24 cm and average 9 cm. Sediment is thickest close to shore and pinches out at about 100 m offshore; there is no alongshore trend in thickness. A crude estimate of the volume of the sediment prism may be obtained by using the average thickness of 9 cm and assuming an average width of 100 m. This yields a total volume of 63 000 m³ for the Canadian deposit along the 7-km industrial reach.

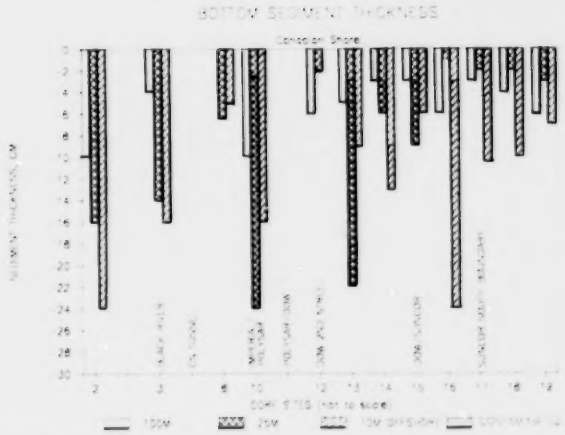

Figure 10. Sediment thickness.

Unconsolidated sediment shows large variations in size from station to station and no consistent pattern of size increase or decrease downriver. Average texture is 63% sand, 32% gravel and 5% silt-clay. Mean grain-size ranges from 0.1 to 9.0 mm and averages 1.7 mm, but most of the sediment is concentrated in two size modes: 4–32 mm (fine gravel) and 0.1–0.5 mm (fine-medium sand).

The size data have important implications with respect to the potential sources of the river sediment. The sand mode falls within the size range that is transported by the river as bedload and that is also available from local erosion of the glacial clay. Its presence is consistent with either or both sources. The gravel mode, however, is too coarse for bedload transport or for derivation from the St. Joseph Till as a residual deposit. It is possible that lenses of coarser till or gravel occur within the St. Joseph unit or that the coarser Black Shale Till is exposed further up the slope than expected. If this were the case, erosion of these units could account for the presence of gravel. Alternatively, the gravel may be fill used to extend or stabilize the shore slope. Indirect evidence of filling is present in aerial photographs, and it is possible that the heterogeneity of grain size and

sediment thickness observed in the cores and underwater television footage reflects the presence of artificial fill rather than natural variability. Confirmation of this would require more data on the shore history and sediment stratigraphy and mineralogy than are currently available. For the moment it should be recognized that some or all of the slope sediment may be artificial, and that its properties will not necessarily reflect the hydraulics of the river or the transport and accumulation rates of bottom sediments.

Lake St. Clair

The size distribution of surface sediment in terms of the relative proportions of gravel, sand and silt-clay is shown in Figure 11. Muddy sand is the major bottom type. Sand and gravel associated with near-surface tills occur along the south coast, well-sorted sand is the delta-front deposit, and clay-rich sediment is restricted to a small area in the west-central part of the basin. The size interval 0.063–0.125 mm is the most common modal size.

Figure 11. Bottom-sediment types.

In 1986, an NWRI coring and echo-sounding survey of Lake St. Clair was undertaken to measure the thickness and volume of the modern sediments and to improve upon the size data for surface sediments. Benthos or impact cores ranging in length from 8 to 216 cm were collected at 31 sites and echo-sounding traverses were run north-south and east-west through the sampling grid to map the sediments acoustically.

Most cores consisted of a thin (less than 10 cm) surface layer of soft sandy mud or muddy sand over stiff glacial clay. Thicker mud (20-30 cm) was present in the west-central part of the main basin and thick sand (30-50 cm) along the delta front. The thickness and size data permit some crude estimates of the total volume of modern sediments and of the volume of polluted sediments. The simple, unweighted average of the thickness data is 13 cm. The product of average thickness and lake area (1114 km^2) yields a total modern-sediment volume of 145 x $10^6 m^3$. Approximately 20% of this, or 30 x 10^6 m^3, is the volume of the silt-clay fraction. Since this is the size range with which pollutants are associated, its volume should place an upper limit on the volume of polluted sediments in the lake.

Tests of acoustic sensors for monitoring sediment accumulation and resuspension were conducted at four sites in the lake during 1986. Analysis of data is incomplete, but preliminary data show negligible change in mid-basin and at the tower site and 3–6 cm changes at Anchor Bay and the Thames River mouth.

St. Lawrence River

Acoustic, sediment descriptive and size data for Lac St-Louis have been combined in Figure 12 to produce a map of the distribution of bottom-sediment types. The limited evidence available on sediment thickness from cores and grab samples suggests a thin (generally less than 10 cm) deposit of modern sediment over stiff glacial clay or bedrock. Grain size is typically sand or gravel in the ship channel and a highly variable mix of sand, silt and clay on the surrounding flats.

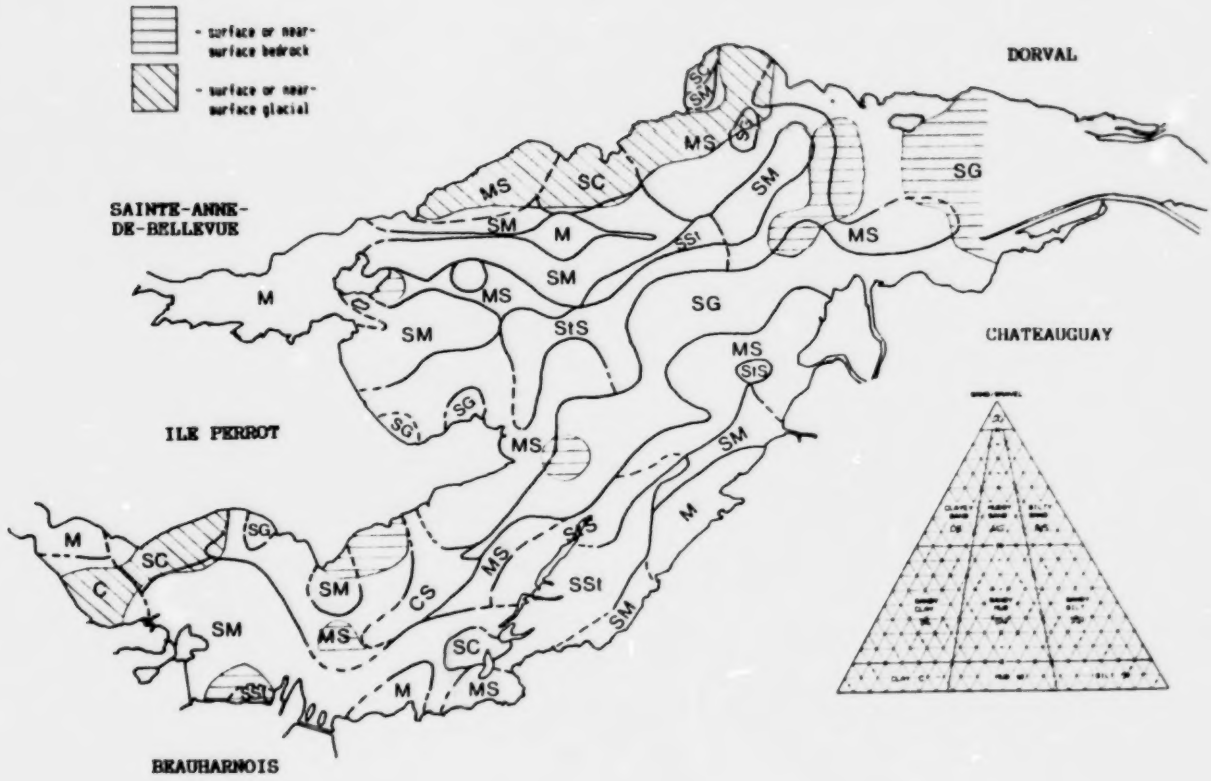

Figure 12. Bottom-sediment types.

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Lake Trout Spawning Habitats

P.G. Sly, Study Leader

P.G. Sly
(Photograph unavailable)

INTRODUCTION

The rehabilitation of the Great Lakes ecosystem is marked by changes in both habitat quality and biological response, and the lake trout has been selected by the Great Lakes Fishery Commission and the International Joint Commission as a key indicator species, representative of sensitive water use values. Lake trout have been heavily stocked in all of the Great Lakes as part of the rehabilitation strategies, but so far, in-lake reproduction by these fish has been very limited. One of the reasons for the lack of successful reproduction by stocked fish may be that habitat degradation continues to limit embryo and juvenile survival. Studies of the lake trout spawning habitat have been initiated to address this concern.

RESEARCH RESULTS

During the fall of 1985, a preliminary study of interstitial water quality in lake trout spawning habitat, in Lake Ontario, demonstrated significant dissolved oxygen (DO) depression. In addition, some high N-ammonia values were observed, and at one site, there was a significant amount of H_2S present. These stressors were potentially lethal to the fall and over-winter development of lake trout embryos. Due to unexpected events elsewhere in the Great Lakes, field support had to be withdrawn and the experimental data remained inconclusive because of excess exposure time. During 1986–87, the field experiments were redesigned to provide comparison of water quality in lake trout spawning substrates in lakes where this species continues to reproduce successfully, in lakes where lake trout are largely supported by hatchery stocking, and in selected sites in Lake Ontario where there is evidence of spawning by stocked fish. Sites were selected in two Algonquin lakes (Opeongo and Louisa), in two New York Finger Lakes (Seneca and Keuka) and at Stony and Yorkshire islands in Lake Ontario.

Bedload and deposited detritus were collected in box samplers (0.5 x 0.5 x 0.1 m) fitted flush with the surface of the cobble-gravel spawning substrates. The boxes were filled with two layers of constant size spheres (artificial substrate) to simulate natural substrate behavior and to provide constant trapping by all sample boxes. Large dialysis chambers were used to measure interstitial water quality. These were made of heavy walled plastic cylinders with internal volumes of about 80 cc. Using a 0.45 μm filter, their equilibrium response time was about four days. These chambers were filled with distilled water and N-purged before placement in the gravel substrates at a depth of about 2.5 cm (one particle layer deep). Temperature, DO, dissolved CO_2 and N-ammonia were measured in the field, based on recoveries at about two-week intervals.

The 1986 field data showed that DO was suppressed during the fall period at all sites. DO was less than 1 mg/L in Seneca Lake and it was also very low during some of the Lake Ontario recoveries. Similarly, N-ammonia was also high at these same sites and the content of non-ionized ammonia was also above lethal levels (hatchery-based data). The CO_2 levels were generally near ambient lake water or slightly above.

Samples of detritus showed that in Seneca Lake the C/N ratio was higher than at most other sites; this appeared to reflect a higher input of terrigenous materials. At most sites, also, the C/N ratio dramatically increased during the latter stages of the fall, indicating the inclusion of partly degraded materials with more locally derived fresh organic material. With the onset of fall winds, bottom sediments at greater depths are prone to reworking. In one case, at least, this resulted in redistribution of sandy sediments containing considerable quantities of sulfides and H_2S. The quantities of detritus were least in the Algonquin lakes and ranged over three orders of magnitude at the Lake Ontario sites. As in 1985 decaying milfoil and *Cladophora* were the main components of the Lake Ontario detritus.

Degradation of excessive quantities of organic matter is therefore a potential threat to the survival of lake trout embryos, although the extent to which this problem occurs over spawning shoals is not known. At all sites, lake trout eggs were recovered in the box samplers, demonstrating that the locations chosen for this study were appropriate. The interstitial water quality of the Algonquin sites was good, and all measured parameters were well within the range necessary to support lake trout embryos. In Seneca Lake, substrate water quality was variable and generally less than adequate. In Lake Ontario, substrate water quality was most variable, and this was directly related to the effects of local wind/wave activity and the proximity of weed beds.

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Great Lakes Connecting Channels

K.L.E. Kaiser, Project Chief

K.L.E. Kaiser

The Great Lakes Connecting Channels Project (GLCCP) addresses the sources, pathways, sinks and effects of organic and inorganic contaminants in the interconnecting channels of the Laurentian Great Lakes. The Laurentian Great Lakes are the world's largest freshwater resource. The entire Great Lakes–St. Lawrence River drainage basin covers over 1 000 000 km^2 (400 000 sq. mi.) and has a population of close to 50 million inhabitants in two Canadian provinces and eight American states. Due to the extensive industrial, agricultural and urban base of this area, organic and inorganic contaminants enter the water from many sources. The interconnecting channels include the St. Clair, Detroit, Niagara, and St. Lawrence rivers and the riverine lakes within these rivers, i.e., lakes St. Clair, St-François, St-Louis, and St-Pierre, as well as the sediment settling areas immediately below the river mouths, i.e., in Lakes Erie and Ontario, and the upper St. Lawrence River estuary. In general, the residence times of water and suspended sediments, and therefore of contaminants, is in the order of hours to days in the rivers, days to weeks in the riverine lakes, and weeks to years in the settling basins. It has been shown that contaminant transport, degradation, volatilization, adsorption, and accumulation rates vary significantly with residence time. Consequently, the dominant processes determining contaminant availability and effects vary significantly between the rivers, riverine lakes and settling basins.

Research is undertaken to determine the pathways and effects of organic and inorganic contaminants in the connecting channels by designing and executing studies on specific contaminant groups and on chemical, microbiological and physical parameters as described in more detail below.

Organic contaminants include a number of chemically related compounds, such as polychlorinated biphenyls, chlorobenzenes, chlorophenols, polynuclear hydrocarbons, volatile halocarbons, and a variety of pesticides and herbicides, generally known as organochlorine compounds. In addition, there are numerous compounds, primarily of industrial origin, which are by-products and wastes of specific plants and processes, such as the manufacture of dyes, paints, and solvents, metal fabrication, plating, chemical and petrochemical plants, and others.

Bacteria, yeasts and fungi are common organisms whose sensitivity to and degradation of contaminants are important factors for the environmental fate and effects of contaminants. Investigations include the determination of distribution and abundance of important micro-organisms, and field and laboratory studies on toxic effects with the Microtox™ test. This part also includes studies on structure-activity relationships for the prediction of contaminant effects.

Toxic metal and metalloid ions (e.g., Cd, Cu, Ni, Pb, Zn, As) as well as hardness, salinity and others (e.g., Ca, Na, pH) are natural constituents of most aquatic systems. However, industrial and urban effluents frequently carry excessive concentrations and/or loadings of such substances. As with organic compounds, their effects are frequently not visible in the rivers, but become apparent in the riverine lakes and settling basins. Therefore, determination of their concentrations, loadings, sources and sinks are important studies in this program.

The effects of physical parameters, including wind and current driven erosion, sedimentation and resuspension of particulates are of considerable importance for the distribution and pathways of adsorbed contaminants. In addition, dissolved materials are transported with the moving water mass. It is therefore important to determine such currents, settling and resuspension rates. These studies also include the modelling of contaminant transport and fate with existing and newly developed computer models.

Structure-Toxicity Relationships for Toxic Organic Chemicals

K.L.E. Kaiser, Study Leader

M.E. Comba
V.S. Palabrica

INTRODUCTION

Chemical pollution of Canadian surface and ground waters is an issue of public concern which has been recognized in several statutes, including the Canada-U.S.A. Agreements on Great Lakes Water Quality, the Environmental Contaminants Act, the Canada Water Act, and a variety of federal-provincial agreements. This project is relevant to both general and regional objectives for toxic substances research.

Many toxic chemicals enter aquatic ecosystems primarily from industrial and municipal effluents. In some localities, leachates from waste dumps (mainly industrial), either directly or through groundwater contamination, and urban runoff are also significant sources of these materials. Numerous examples for each of these sources exist, such as on the St. Clair, Niagara, and St. Lawrence rivers. Several thousand contaminants have been identified in water, sediments, air and biota, but only a few of these compounds have adequately been defined in terms of their environmental pathways and effects. Therefore, there is an urgent need to determine these contaminant characteristics.

This program addresses existing knowledge gaps on the properties and pathways (partitioning, bioaccumulation, degradation, persistence, volatilization), and fates and effects (transformation, deactivation, acute and sublethal toxicities, chronic exposure effects) of known or suspected environmental contaminants in surface and ground water. As the rate of introduction and observation of new compounds exceeds that of resolution of their environmental processes effects, the research program includes structure-activity relationships which allow the estimation of such characteristics both from structural parameters and the properties of similar compounds.

RESEARCH RESULTS

In June 1986, the 2nd International Workshop on QSAR (Quantitative-Structure-Activity Relationships) was held at McMaster University, Hamilton, under the chairmanship of K.L.E. Kaiser. Some 50 participants from 12 countries presented and discussed new results on structure-toxicity, structure-biodegradation and structure-bioaccumulation studies. The proceedings of this symposium have been edited and have been submitted for publication.

The results of our investigations into the toxicities for *Photobacterium phosphoreum* (using the Microtox™ test) of over 100 monosubstituted and over 130 1,4-disubstituted benzene derivatives were presented at the workshop. It was shown that the toxicities of virtually all of these compounds, which range over five orders of magnitude on a molar basis, can be predicted from chemical and physical properties of these compounds. These results should be applicable to many other compounds of a similar chemical structure and will be helpful for the screening of chemicals for environmental hazard potential. Figure 13 gives a plot of the observed toxicities of monosubstituted benzene derivatives versus those of the corresponding p-chlorosubstituted compounds, indicating a close relationship between these values.

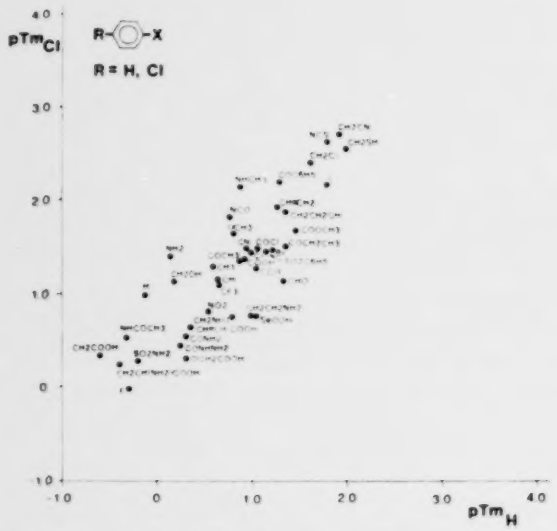

Figure 13. Plot of the toxicities of monosubstituted benzene derivatives (pTm_H) of the general formula H-C_6H_4-X versus the toxicities of the corresponding para-chlorosubstituted benzene derivatives (pTm_{Cl}) of the general formula Cl-C_6H_4-X; toxicities measured with the Microtox test; axes are logarithims of inverse milli-molar concentrations.

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Volatile Contaminants in the Great Lakes Connecting Channels

K.L.E. Kaiser, Study Leader

M.E. Comba
V.S. Palabrica
K.R. Lum

INTRODUCTION

The Great Lakes and connecting channels, especially the Niagara, Detroit and St. Clair rivers are recipients of many toxic subtances from industrial and municipal origins. Building upon previous observations on generally increased levels of volatile chlorocarbons, such as carbon tetrachloride and tetrachlorethylene in association with other contaminants, and based on the discovery of liquid chlorocarbon puddles on the bottom of the St. Clair River, field studies were extended to include the St. Lawrence River and the riverine lakes.

RESEARCH RESULTS

In October 1985 and July 1986, over 200 small-volume water samples were collected from the St. Lawrence River between Cornwall, Ontario and Tadoussac, Quebec. Analysis of these samples for volatile halocarbons indicated a number of areas with significantly increased levels of several compounds including carbon tetrachloride, tetrachlorethylene (Fig. 14), 1, 1,1-trichlorethane, trichlorethylene, and chloroform. Most of these zones are downstream of known industrial and municipal effluent sources and/or tributaries which receive such effluents. The results indicate areas of potentially impaired water quality and are presently being investigated more thoroughly.

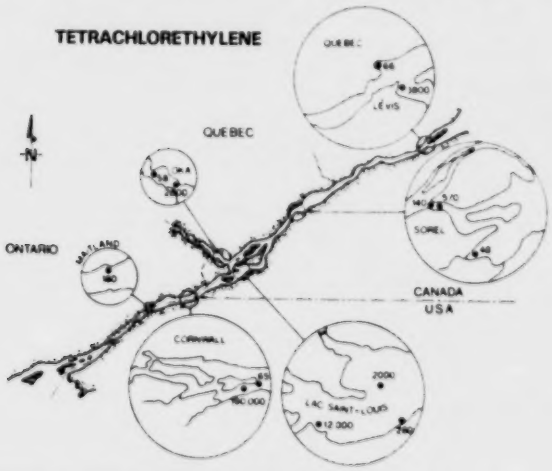

Figure 14. Tetrachlorethylene concentrations in selected surface water samples of the St. Lawrence River, in October 1985, values in ng/L, from Lum and Kaiser (1986).

At pre-selected sites, some 30 large-volume water samples were also collected and separated into the dissolved and suspended particulate fractions by centrifugation. These samples are still being analyzed, but preliminary results indicate the presence of several classes of organic contaminants in both dissolved and particulate fractions.

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Predicting the Fate of Toxic Contaminants in the Aquatic Environment

E. Halfon, Study Leader

B.G. Oliver
W.M. Schertzer
T.J. Simons

E. Halfon

INTRODUCTION

The systems ecology research effort in 1986/87 focused on two main research areas. The first research area was the continuing development and improvement of the toxic contaminants fate model TOXFATE. This computer model was applied to predict the fate of chlorobenzenes and PCBs in Lake Ontario and to predict the fate of halocarbons, including perchlorethylene, in Lake St. Clair. The second research area was the development of the new ranking method, POSET, which was applied to two different problems: ranking of toxic contaminants according to environmental hazard and ranking of waste disposal sites on the shores of the Upper Great Lakes Connecting Channels.

During the year, three other projects were also performed. The first project was the preparation of a large detailed report to explain to other government employees, not expert in systems ecology and mathematical modelling, how systems methodologies could be applied to plan research projects and monitoring studies. The second project was an analysis of the Yamaska River watershed from a systems point of view. The rationale for this project was the planned establishment of the Hyundai car assembly plant near the resort area of Bromont, Quebec. Once this plant begins operation, discharges of heavy metals and organic contaminants are expected to take place. The final project was a theoretical analysis of the volatilization process in lakes. This project originated from the fact that some scientists at NWRI believe that some toxic contaminants, such as chlorobenzenes, tend to leave the Great Lakes by volatilization at high rates. Other scientists believe that this volatilization process does not take place at fast rates and therefore this process is relatively not important as a removal pathway. In this study the assumptions at the basis of two volatilization models were analyzed and predictions compared.

The Mathematical Model

TOXFATE is a contaminant fate model which integrates information on the properties of a chemical, such as molecular weight, solubility, vapor pressure, and the octanol-water partition coefficient, with information about the environment where the chemical is found, such as water circulation, wind speed, the amount of suspended solids, etc. The model can be used to predict concentrations at different locations and estimate the importance of removal processes such as volatilization. TOXFATE includes parameters that quantify degradation processes such as photolysis, oxidation, hydrolysis, and biodegradation and biotransformation. The model also computes bioaccumulation and biomagnification. TOXFATE simulates the time-varying concentrations of a toxic contaminant in the water column. The equations can be parameterized to represent a variety of contaminants and the model is formalized as a system of ordinary differential equations. The state variables (Fig. 15) are organic contaminant concentrations in suspended clay and colloidal matter, suspended silt, suspended sand, water, plankton, and fish, bottom sediments and benthos compartments. TOXFATE also includes a resuspension submodel. Most process relationships are nonlinear and reflect the continuous movement of the contaminants between sediments, water and biota. The transport processes of advection in water are handled by a box model which includes information about the water circulation computed by hydrodynamic models; the pollutant is assumed to be immediately and completely mixed within each spatial cell.

Figure 15. Structure and state variables of the model TOXFATE. The arrows indicate the possible flow of toxic contaminants between compartments. The state variables are the concentrations of the contaminant in each part of the ecosystem.

RESEARCH RESULTS

Lake St. Clair

The contaminant fate model TOXFATE has been coupled with a hydrodynamic model of Lake St. Clair. The purpose of this research is to predict the behavior of seven volatile halocarbons, bromochloromethane, carbon tetrachloride, chloroform, freon 12, 1,1,1-trichlorethane, trichlorethylene and tetrachlorethylene in Lake St. Clair and to describe the contaminant plumes on the lake. Simulations are compared with contaminant concentrations data collected June 18-21, 1984, at 67 stations in Lake St. Clair. Whereas the data present only a four-day composite picture of the seven halocarbons, the computer model computes the contaminant plumes on an hourly basis. Given the spatial resolution of the lake, divided into a 2 x 2 km grid, the model could be used to simulate the fate in the lake of spills which might occur on the lake shores or upstream in the St. Clair River. The contaminant data collection is only a snapshot of an event continuously taking place in the lake, mainly the flow of organics from the St. Clair River into the lake and on to the Detroit River.

Contaminant Plume Analysis–Freon 12

Figures 16 and 17 show the computed plumes of freon 12 and trichlorethylene at noon on June 18, 1984, and on June 21, 1984. Figure 16 shows that the plume off the Thames River started to develop only on June 17 and 18 following an increase of the Thames River flow. This plume developed over the next three days, and on June 21 it expanded westward past the Belle River on the south shore. Kaiser and Comba sampled that part of the lake on June 19 and therefore detected the plume in its expanding stage. On June 18 and 19 the wind was from the southwest and therefore the freon 12 plume from the Thames River tended to stay near the east coast of the lake. On the following two days, June 20 and 21, the wind changed from the northeast and, given the increased flow in the Thames River, the freon 12 plume moved south and west relatively fast. The discovery of a freon 12 plume from the Thames River was therefore coincidental with the sudden flow increase in the Thames River from an average of 100 m^3/s to 213 m^3/s on June 18 and to 545 m^3/s on June 20. The flow in the St. Clair River was 6633 m^3/s.

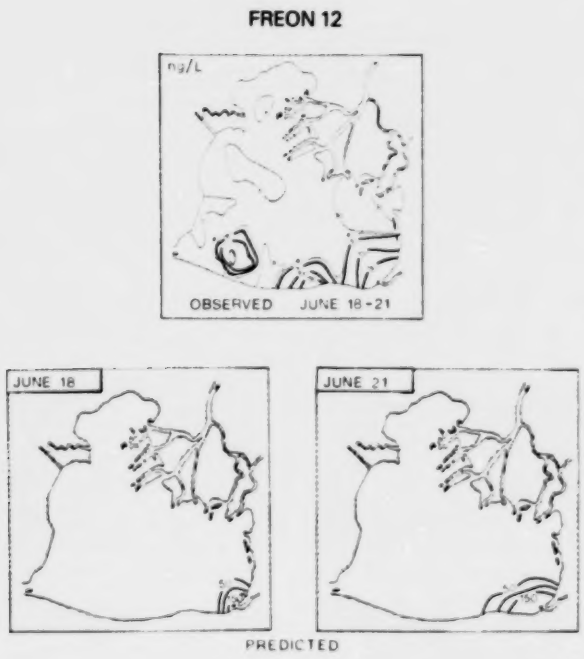

Figure 16. Composite picture of observed concentrations in water (ng/L) of freon 12 during the period 18-21 June 1984 and predicted concentrations on June 18 and June 21 using the model TOXFATE.

Figure 17. Composite picture of observed concentrations in water (ng/L) of trichlorethylene during the period 18-21 June 1984 and predicted concentrations on June 18 and June 21 using the model TOXFATE.

Contaminant Plume Analysis–Trichlorethylene

Figure 17 shows the computed plumes of trichlorethylene on June 18 and 21. An analysis of Figure 17 shows the development of a plume of trichlorethylene from the Thames River over the four days. Figure 17 also shows that due to wind conditions, the plume from the Chenal Ecarté tended to stay near the eastern shore of the lake during June 18 and 19 and to move westerly on June 20 and 21.

Lake Ontario

The fate model TOXFATE is also used to predict the fate of four chlorobenzenes which have entered Lake Ontario from the Niagara River since 1909. They are 1,2,4-trichlorobenzene (1,2,4-TCB), 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB), pentachlorobenzene (QCB) and hexachlorobenzene (HCB).

Simulations show that on average about 31% of HCB loadings and 43% to 76% of the other three chlorobenzenes are lost from the lake through volatilization while field estimates range between 38% and 93%. The model predicts that about 14% of 1,2,4-TCB loadings remain in the bottom sediments while 21% to 61% of the other chemicals do; field estimates range between 4% and 57%. Despite total chemical inputs to the lake of 15 000 to 310 000 kg, the water faction in 1983 contains only a minute proportion, namely 30 to 1000 kg for each chemical over the whole lake, resulting in very low water concentrations on the order of 0.02, for HCB to 0.7 ng/L for 1,2,4-TCB. Concentrations in trout range from 3–6 ng/g dry weight for 1,2,4-TCB to 65-130 ng/g for HCB. Fish bioconcentration factors over water range from 5800 for 1,2,4-TCB to 2 4000 000 for HCB. A novel fish model has been developed to describe the large range in bioconcentration factors of the different chlorobenzenes.

One question that was investigated with the model is the time frame that it would take for some contaminants to be permanently buried in the bottom sediments if loadings were completely stopped. Two chemicals, HCB and 1,2,4-TCB, were chosen as representative of relatively persistent and more volatile compounds. 1,2,4-TCB is very volatile and therefore only about 4% to 14% of the loadings are in the bottom sediments. If loadings were completely stopped, it would take about 38 years for the four chlorobenzenes to be buried under 8 cm of clean sediments.

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Physical Measurements in Lake St. Clair and the St. Lawrence River

P.F. Hamblin, Study Leader

C.R. Murthy, F.M. Boyce, F. Chiocchio, K.C. Miners, D.B. Robertson and C.R. McCrimmon (Contract)

P.F. Hamblin

INTRODUCTION

Lake St. Clair

In the field season of 1986/87, supplementary physical data were collected in Lake St. Clair to those in the previous year along with several U.S. research teams. This program of research was aimed at determining the conditions for the resuspension of suspended sediments and their transport and thereby the possible exports of sediment from Lake St. Clair to the Detroit River. In this way it was hoped that the fate of halogenated organics discharged into the St. Clair River may be known. The focus of the 1986/87 field program was the continuous recording of suspended sediment concentration and supporting current data at several levels in the water column and at several locations in the region of maximum fetch to the prevailing winds. As well, waves, surface meteorology and lake-wide suspended sediment surveys completed our field program. As in 1985, a vertical array of sediment traps considered to be indicative of the horizontal sediment flux were monitored over eight episodes.

St. Lawrence River

In the field season of 1986/87, physical measurements including moored current meters at three locations and several thermal mapping surveys were undertaken in eastern Lake Ontario with the objective of determining the circulation and water masses supplying the outflow to the St. Lawrence River.

In the region of the upper estuary of the St. Lawrence River previous physical studies were reviewed and basic physical data were collected in support of the chemical sampling program in the estuary during the field season of 1986/87.

RESEARCH RESULTS

Lake St. Clair

The collections from the horizontal flux traps were analyzed in the laboratory for particle size distributions, settling velocity and percentage organic content. During the most stormy periods, the particle size distribution is bimodal at the southeastern corner of Lake St. Clair with principal modes of coarse and fine silt (Fig. 18). Perhaps on

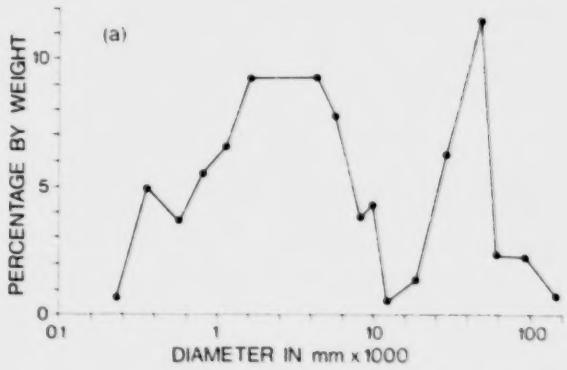

Figure 18. Typical grain size distribution in southeast Lake St. Clair.

account of the bimodal nature of the suspended sediment grain size distribution, the relation between optical transmission and suspended sediment concentration has considerable scatter. Wave statistics at several locations are in reasonable agreement during major events despite the different methods of measurement. Comparison of significant orbital velocities close to the bottom inferred from the surface wave observations are in good agreement with direct measurements of the acoustical current meters. Near bottom orbital velocities increase markedly within several kilometres of the downwind shoreline and appear to be more strongly correlated with the abrupt increase in suspended sediment concentration than bottom shear stress which lags the other data. In the 1986 data set

elevated levels of suspended sediment concentration did not occur at the Windsor water treatment plant intake during the observational period. Indications that significant export of sediment from Lake St. Clair is restricted to occurrences of waves of at least 50 cm height impinging on the southwestern shoreline, are evident for intake turbidities at Windsor during 1985 (Fig. 19).

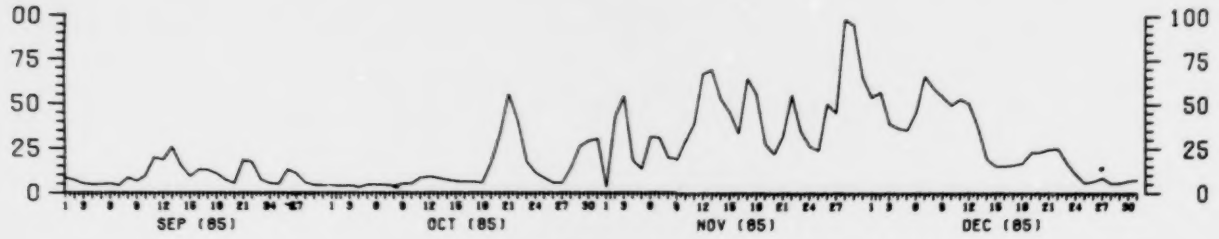

Figure 19. Water intake turbidities, Windsor.

St. Lawrence River

Preliminary indications are that upwelling of cold bottom water in the Kingston Basin of Lake Ontario plays a significant role in circulation near the entrance to the St. Lawrence River.

A review of past studies in upper estuary of the St. Lawrence River indicated that a capability to simulate physical processes is limited to surface tides alone and that the current field, salinity and temperature distributions as well may be required to determine the transport of contaminants. These features must be measured along with the chemical observations. Prior physical studies concerned with determining the physical factors responsible for suspended sediment transport, resuspension, and deposition are extremely limited in the upper estuary. A new mechanism for the recycling of suspended sediments and possibly contaminants has been observed in the anchor station data. The results of a model for the vertical transport of suspended sediments in the upper estuary demonstrate that the principal cause for this tidal pumping mechanism is tidally induced fluctuations in the vertical diffusive transports, which in turn are related to the intrusion of the salt wedge during the flood portion of the tidal cycle. Particle size of the dominant fraction of suspended sediment inferred from the transport model and field observation is in close agreement with other studies. The horizontal and vertical sediment fluxes at one anchor station are summarized in the form of a two component model (Fig. 20). The residence time for particles resuspended at the bottom during peak tidal flow is estimated to be 10 h, which may be compared to the overall settling time of 23 h.

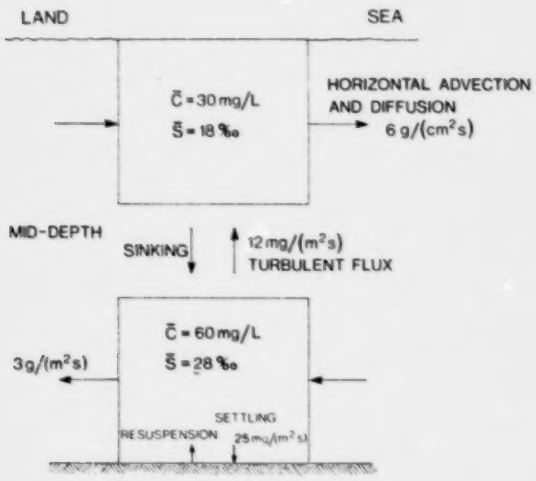

Figure 20. General model of horizontal and vertical fluxes of sediment in the upper estuary of the St. Lawrence River.

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Distribution of Yeast and Fungi and their Response to Contaminants

K. Kwasniewska, Study Leader

K. Kwasniewska

INTRODUCTION

As yeasts are eucaryotic organisms, they can serve as model organisms for research on environmental contaminants. Their existence under both aerobic and anaerobic conditions (oxidative and fermentative yeasts) and their high salt and sugar tolerance make them important indicators for environmental enrichment (pollution) and contamination by toxic chemicals.

Since the studies are related, it was decided to investigate both the presence and density of the organisms as they affect biodegradation and accumulation of chemicals.

The preliminary survey of the horizontal and vertical distribution of yeasts, fungi and some bacteria in Lake St. Clair water and in Lake Erie sediment has been completed.

RESEARCH RESULTS

In June 1984, 67 100-mL subsurface water samples were collected from stations throughout Lake St. Clair. Organisms from water samples were isolated by filtration through membrane filters and cultured on defined media.

For isolation of these organisms from sediment, different techniques were applied. Subsequently, the colonies of representative predominant yeasts, fungi and some bacteria were tentatively identified. The report on distribution of yeasts, fungi and bacteria in St. Clair water have been presented. From Figure 21 it can be seen that the great majority of yeasts and fungi occur primarily in nearshore zones and near several tributaries and may imply a close relationship between water pollution and yeasts population.

We have also undertaken preliminary investigations of the distribution and abundance of yeasts in the St. Lawrence River in 1985 and 1986.

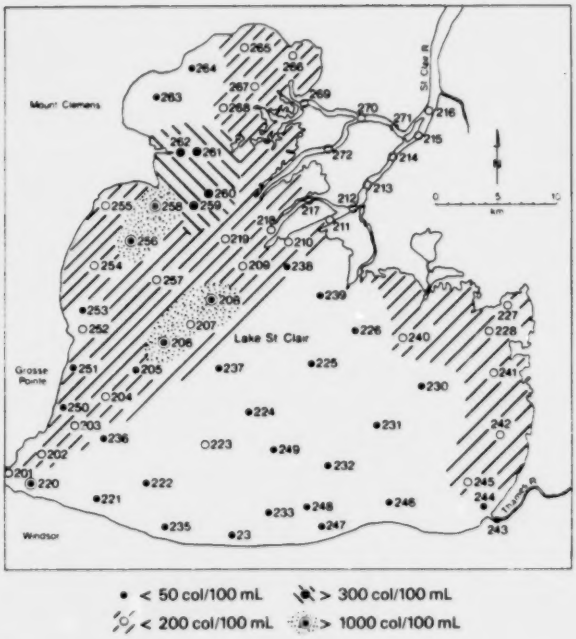

Figure 21. Densities of yeasts in Lake St. Clair water.

In addition, we will continue the work on the toxicity, biodegradation and/or accumulation of selected model contaminants by prevalent yeasts and fungi.

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Biogeochemical Cycling of Metals with Special Reference to the St. Lawrence River

K.R. Lum, Study Leader

M. Callaghan
E.A. Kokotich

K.R. Lum

INTRODUCTION

The nearly 3000 km of shoreline along the St. Lawrence River are the home of some of Canada's largest cities and factories, the majority of which discharge their wastewater directly into the river with little or no treatment. Concern for contamination is exacerbated by the fact that the St. Lawrence River is the end unit of the aquatic ecosystem-corridor through which toxic chemicals are ultimately discharged to the Gulf of St. Lawrence. This river provides a classic case of management problems resulting from a variety of conflicting uses. For example, its shores are now the home of 80% of Quebec's population and nearly five million Quebecers draw their drinking water from the river. The St. Lawrence has been and still is a vital factor in Canada's social and economic development, both as a navigable waterway and as a source of water for industrial needs. The river and its inshore areas are also a rich and diversified environment for freshwater and marine fauna and wildlife, and thus provide recreation for many thousands.

This study is aimed at measuring the distribution of toxic chemicals, including a wide range of metals, in the St. Lawrence River to determine where water quality is impaired, for what chemicals and over what area. Because contaminant retention is expected to be a transient feature of the river up to Quebec City, the project will focus as well on changes in environmental mobility, bioavailability and deposition at the freshwater-saltwater interface in the Upper Estuary.

The second major cruise on the St. Lawrence River was successfully completed during June-July of 1986. Relative to the *Limnos* expedition of October 1985, we were able to sample three anchor stations intensively in the upper estuary between Quebec City and the mouth of the Saguenay River.

The results to date on the distribution of volatile hydrocarbons (VHCs) and dissolved and particulate cadmium in the river from the outflow of Lake Ontario to Quebec City have been published. Although the data show local impairment in water quality, none of the VHC or cadmium concentrations exceed water quality guidelines or objectives. Nor should the concentrations have any acute toxic effect on aquatic organisms. Our results indicate that there are major sources of VHCs and cadmium in Quebec (see Fig. 22 for example). Inputs on the southwestern portion of Lac St-Louis may be a major source of perchlorethylene, and effluents in the vicinity of the Montreal STP may be a major source of cadmium. U.S. tributaries, e.g., the Grassy River, may also be a significant source of VHCs.

Figure 22. Dissolved cadmium concentrations in selected surface water samples of the St. Lawrence River, in May 1985, values in ng L^{-1}.

During the year, the validation of an analytical method for cadmium suitable for fresh as well as estuarine waters was completed and a review of cadmium in fresh water prepared. Mass balance budget calculations were done for Lakes Erie and Ontario. One result of this exercise was a revised atmospheric loading estimate for each of these lakes. The calculations show that inputs of cadmium are almost completely balanced by outputs.

For the St. Lawrence River, the average concentration of dissolved cadmium was determined to be 15 ng L^{-1}, and dissolved forms represent about 60% of the total cadmium transported by the river. By comparison, dissolved cadmium in the Mississippi River is about 10% as a result of the greater importance of particle-mediated processes in this river. Although an average distribution coefficient was obtained from many measurements of dissolved and particulate cadmium, its usefulness as a predictive tool is limited presumably because of kinetic factors. Flux calculations indicate that the discharge of dissolved and particulate cadmium is much lower than previous estimates. This result is primarily due to improved sampling and analytical methodology.

A study of the bioavailability of Cd, Pb and Zn in wet and dry deposition showed that, for example, the average amount of Cd deposited in the precipitation events sampled at five U.S. sites was ten times the amount deposited at the Canadian sites sampled. Water-soluble forms dominated the "particulate-speciation" of the three metals in atmospheric particulate matter from south-central Ontario. This ease of solubility suggests that the greatest impact in terrestrial and aquatic systems will likely occur at interfaces, e.g., at forest canopies and at the air-water interface.

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Niagara River Toxics Transport in Lake Ontario

C.R. Murthy, Study Leader

D.C.L. Lam
K.C. Miners

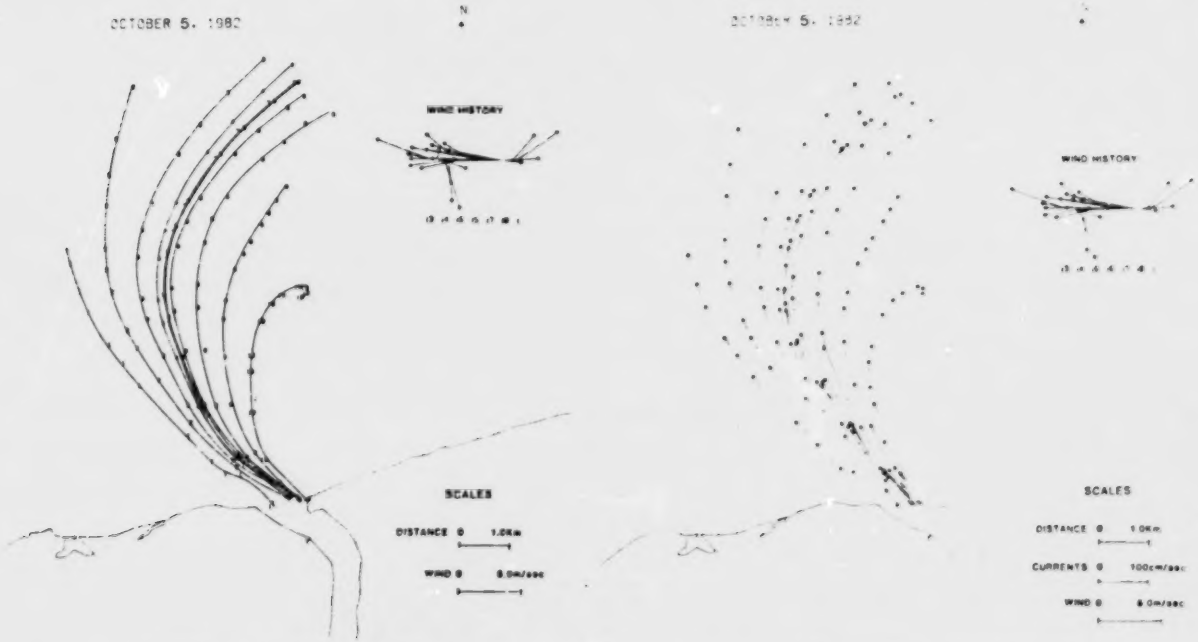
C.R. Murthy

INTRODUCTION

With an inflow of 7000 m^3/s, the Niagara River is the largest single input of materials into Lake Ontario. In recent years, there has been much concern about the transport, distribution, pathways and fate of toxic contaminants entering the lake from the Niagara River. This study is devoted to the delineation of the physical characteristics of the Niagara River Plume in Lake Ontario and to the development and evaluation of contaminant transport model to simulate the distribution, fate and pathways of selected contaminants entering Lake Ontario via the Niagara River.

RESEARCH RESULTS

The physical characteristics of the Niagara River Plume can be broadly classified as nearfield and farfield. The nearfield mixing characteristics are dominated by the initial momentum and buoyancy of the river plume. The river plume merely spreads over the shallow sand bar and is completely mixed vertically due to self-generated plume turbulence and wind-generated turbulence. This initial phase is restricted to the shallow sand bar area as can be seen from an order of magnitude reduction of horizontal velocities from 200°cm^{-1} at the river mouth to about 20 $cm^{\bullet-1}$ at the edge of the bar. Figure 23 shows the



LAGRANGIAN TRAJECTORY HORIZONTAL VELOCITY FIELD

Figure 23. Lagrangian trajectory and horizontal velocity field of the Niagara River Plume, 5 October 1982.

horizontal flow velocities in the Niagara River Plume as it merges with the lake, inferred from a carefully conducted Lagrangian drifter experiment in the nearfield. The vertically well-mixed river plume over the sand bar area as seen from the temperature cross-sections (Figures 24a and b) illustrates that the nearfield influences are observed approximately 5 km from the river mouth. Interaction of the well-mixed weakly buoyant river plume at the edge of the bar creates some large-scale isotherm displacements indicating intense vertical mixing activity. With the intrusion of colder water from deeper depths of the lake, a sharp thermal front is generated and maintained in the vicinity of the bar edge. The evolution of the thermal front from the early spring warming to late fall can be identified in the vertical temperature cross-sectional data in all the experiments.

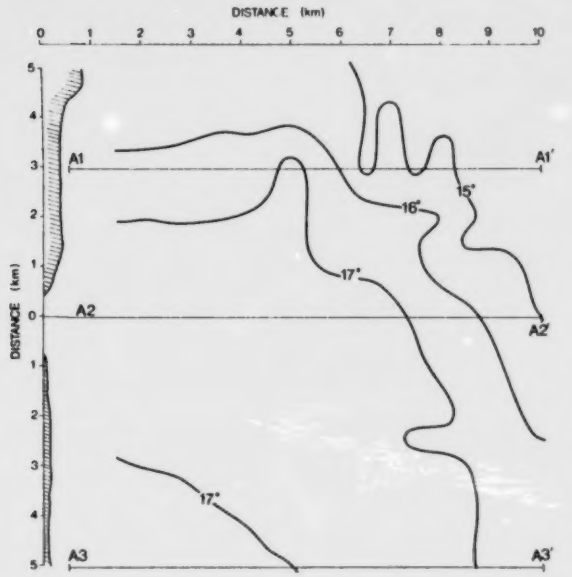


Figure 24a. Horizontal distribution of averaged temperatures: Niagara River Plume, upper layer (10 m of thickness), 5-7 October, 1982.

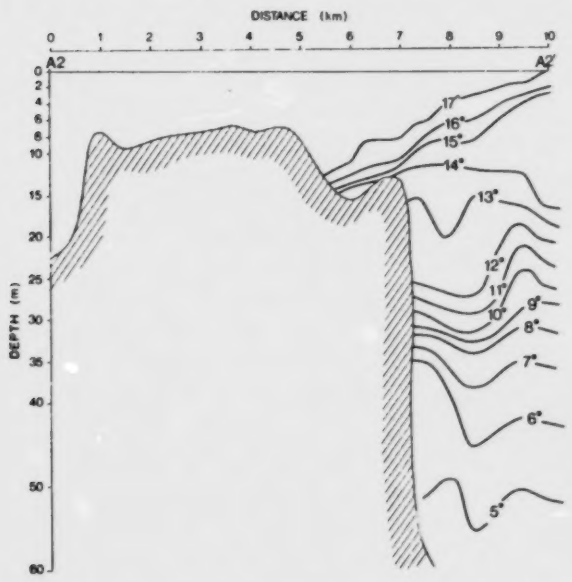


Figure 24b. Average temperatures in the vertical cross-section A2 - A2' 5-7 October 1982.

The farfield mixing characteristics of the river plume are controlled by the prevailing winds and the lakewide circulation. Figure 25a shows the farfield characteristics and the long-term fate of the Niagara River Plume and its relationship to prevailing winds and lakewide circulation constructed from Lagrangian flow data from satellite-tracked drifters. Although the drifters were released at the same point and at the same time, their trajectories are totally different, thus providing a glimpse of the effect of small-scale turbulent motions in lakes and the unpredictability of water displacement in a deterministic manner. At the same time, however, the drifter tracks also exhibit clear evidence of the significant effect of large-scale current regimes. Large-scale current regimes determine the actual displacements of the drafters. These results reveal the remarkable variability of the Niagara River Plume. Two significant long-term effects of the river plume in Lake Ontario are evident: the Niagara River Plume sweeps across the western basin on numerous occasions, and the river plume is frequently trapped in the belt of eastward boundary current along the south shore. It is of interest to look at the correlation between these observed effects and the distribution of toxic con-

Figure 25a. Farfield characteristics of the Niagara River Plume inferred from the satellite tracked drifters.

taminants. The sediments integrate the long-term effects and therefore the distribution of toxic contaminants in the sediments of Lake Ontario will be a true reflection of farfield effects of the Niagara River Plume. Figure 25b shows an example of mercury distribution in the sediments of Lake Ontario attributed to the Niagara River Plume (Thomas 1983). The dominating effect of the year-round belt of the strong boundary current along the south shore as well as the

westward displacement of the Niagara River Plume are clearly evident and thus confirming the farfield characteristics of the Niagara in the lake inferred from the Lagrangian satellite-tracked drifter experiments.

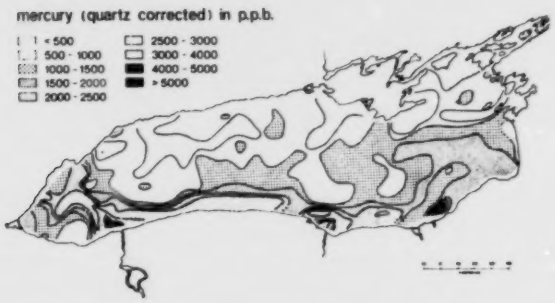


Figure 25b. Mercury distribution in the sediments of Lake Ontario attributed to the Niagara River Plume.

Contaminant transport models to simulate the transport, distribution and pathways of some selected contaminants entering Lake Ontario via the Niagara River are currently being developed and evaluated using a physical and toxics data base.

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Eutrophication Model of the Upper Great Lakes Connecting Channels (UGLCCS)

T.J. Simons, Study Leader

W.M. Schertzer

T.J. Simons

INTRODUCTION

The Upper Great Lakes Connecting Channels Study on Lake St. Clair was conducted over the period May-November 1985. The overall objective of this investigation was to model material transport and sediment-water exchanges. Several specific objectives for 1986/87 were outlined, including the following:

1. To model water movement by numerical methods and to verify the model against extensive current meter observations.

2. To evaluate the various components of the water balance including water level changes due to winds.

3. To model wind-generated waves and to verify the model against wave measurements.

4. To model sediment resuspension induced by currents, waves and turbulence and to verify against measurements.

RESEARCH RESULTS

Preliminary estimates of the major hydrological components of the Lake St. Clair system were conducted for the period June 5 to November 6, 1985. The St. Clair and Detroit rivers dominate the water budget with average flow rates of 6309 m^3/s and 6492 m^3/s, respectively, over the measurement period. Runoff, precipitation and evaporation represent average exchanges of 76 m^3/s, 41 m^3/s, and 38 m^3/s, respectively. These rates are significantly higher than long-term averages attributable to higher water levels and wetter than usual conditions.

Modelling material transport and sediment water exchanges in Lake St. Clair requires adequate knowledge of water movements. With increased concern regarding contaminant exchanges at the sediment water interface, it is no longer sufficient to know the mass transport over a water column but it has become necessary to evaluate the vertical structure of flow and, especially, the current near the bottom. Numerical model calculations based on the Ekman theory for finite water depth are performed to assess the water movements emphasizing wind, depth and hydraulic flow characteristics. Modifications to the conventional steady-state Ekman model are introduced to provide better estimates of current speeds near the bottom. Figure 26 shows streamlines of the hydraulic flow

Figure 26. Computed streamlines (100 m^3/s) of hydraulic flow and corresponding empirical model currents for three classes of wind mixing.

Dr. T.J. Simons (1939-1987) contributed significantly to the advancement of limnological research and his work was well recognized by major research agencies around the world. Dr. Simons was awarded with the Chandler-Misener Award of the International Association of Great Lakes Research in 1972, 1973, and 1976 as well as receiving an Award of Merit from the Canadian Public Service in 1980.

Among his accomplishments were the development of three-dimensional hydrodynamical models and water quality models of lakes. His current investigations on Lake St. Clair display the excellence and dedication which he portrayed in all of his endeavours.

associated with the inflow of the St. Clair River and the outflow of the Detroit River. The streamlines separate the flows from the North Channel, the Middle Channel, the south bend of the South Channel and the St. Clair cut-off. Empirical model currents have been entered at the locations of the measurement stations. For higher values of wind mixing, these currents are seen to be aligned with the vertical mean flow, while for lower wind mixing they deviate to the left. The hydraulic flow is seen to turn south upon leaving the St. Clair River before heading west to the Detroit River. Circulations are derived using the Ekman model for winds blowing along normal to the main transect which indicate topographic effects on the circulation patterns.

Interest in the problem of wind induced changes in water level along the Great Lakes has been enhanced by the record high water levels during 1986. Changes of water level caused by wind are most pronounced in shallow lakes such as Lake St. Clair. On the basis of water level measurements at St. Clair Shores and Belle River from June 1 to November 30, 1985, a two-dimensional hydrodynamic model was used to produce simulations of wind-induced changes of water level. Figure 27 shows a regression of hourly values of observed vs. computed set up (Belle River–St. Clair Shores) for wind directions within 30 degrees of the set up line and for different stability classes. Further analysis of the lake set up shows that the free surface oscillations in Lake St. Clair are strongly damped. The lake settles down to a steady-state due to the large frictional damping associated with the shallow water depth. Consequently, it may be concluded that Lake St. Clair may usually be in a quasi-steady balance with wind forcing.

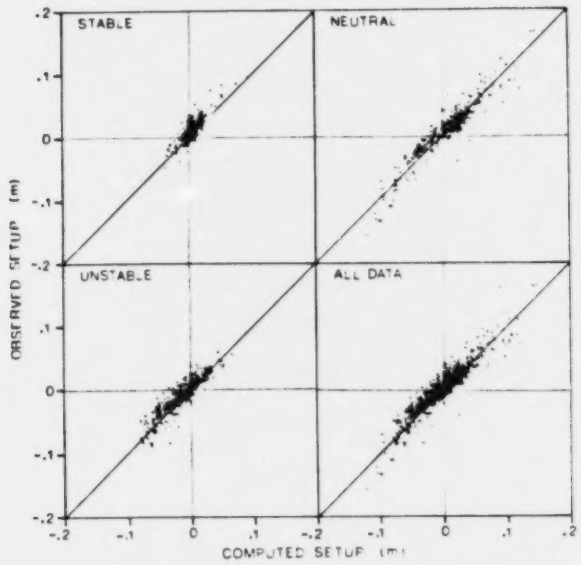

Figure 27. Observed vs. computed set up (Belle River - St. Clair Shores) for class of wind directions within 30 degrees of set up line and for different stability classes.

Wave and sediment measurements conducted on Lake St. Clair were used to arrive at a dynamic sediment resuspension model which was used to simulate sedimentation rates. Model development required determining a dynamic relationship between suspended matter and wave orbital velocity. Based on a dynamic relationship between suspended matter and wave orbital velocity, sediment resuspension is computed and integration of the results provides a solution for the accumulated sedimentation for each sediment trap interval. Figure 28 shows observed and computed sedimentation rates averaged over the time interval between sediment trap retrievals.

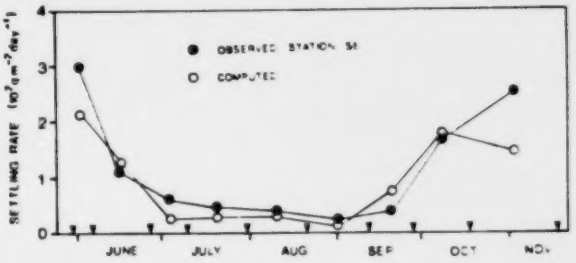

Figure 28. Measured and computed sedimentation rate at Station S6. Model results based on predicted waves.

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Air-Water Interactions

W.M.J. Strachan, Project Chief

W.M.J. Strachan

This project involves all aspects of chemical and physical atmosphere-(lake) water interactions. At present there are two dominant foci. The first is deposition from and volatilization to the atmosphere of toxic organic and other chemicals. The second is the role that climatic changes play in controlling lakes such as the Great Lakes and their water quality, and the influence large lakes have on climate.

Atmospheric deposition of toxic chemicals represents a major input of these substances to the Canadian ecosystem. Various parameters governing their wet, dry and vapor phase transfers to and from surface waters are determined. This, together with information on process rates and hydrological aspects of the lake systems under study, are incorporated into models. Study areas at present are the Turkey Lakes (near Sault Ste. Marie, Lake Superior region) and Lake Ontario. Related activities include the examination of wetland and bog ground cover as biomonitors of atmospheric deposition, particularly of metals near smelters.

Climatic changes (temperature, amount of precipitation and evaporation, presence of entrained material) greatly influence water quality and quantity. Current efforts are on the development of paleolimnological indicators of climatic changes and on determining the hydrological balances of the lower lakes. Calcitic shells of benthic invertebrates found in cores of lake sediments are being examined for their utility as indicators; this activity is well advanced for the Prairie region and similar work is commencing in the Great Lakes. Climatic effects on lake stratification cycles and on water quality are near completion on the lower Great Lakes, and investigations are beginning on the long-term hydrological balance of Lake Ontario.

Atmospheric Deposition of Organic Pollutants

W.M.J. Strachan, Study Leader

INTRODUCTION

The program of investigation into the behavior of persistent organic contaminants continued in the fiscal year 1986/87. In addition to the ongoing rain program, two new aspects were introduced: a laboratory study to determine the bulk transfer coefficients of a number of representative compounds, and a field study to obtain a comprehensive data set for a small lake system. All three aspects of the program are intended to provide the Department of the Environment with an accounting ability for the distribution of these chemicals in aquatic related systems.

RESEARCH RESULTS

Atmospheric Deposition in Rain

Triplicate samples were collected from two research sites: Mount Robson (east-central British Columbia) and Kanaka Creek (in the Fraser estuary near Vancouver, British Columbia). These were analyzed for 17 organochlorine pesticides, PCBs and a selection of polynuclear aromatic hydrocarbons (PAHs) and chlorinated benzenes. In addition, single samples were collected at three sites in the prairie provinces (Suffield, Alberta; Cree Lake, Saskatchewan; and McCreary, Manitoba) and at ten locations around the Great Lakes (Sibley, Rossport, Wawa and Turkey Lake on Lake Superior, South Baymouth and Sarnia on Lake Huron, Pelee Island and Long Point on Lake Erie and Niagara-on-the-Lake and Wolfe Island on Lake Ontario). Preliminary results are presented in the accompanying Table 1. Analysis of the samples from the research stations are not complete nor are the last samples from the routine (single sampler) stations. The volume-weighted means presented are the result of 3–5 samples received during the entire wetfall period at the named sites.

Table 1. Rain Data for Ontario and Western and Northern Regions - 1986.

Volume-Weighted Mean Concentration (ng/L)

	Lake Superior				Lake Huron		Lake Erie		Lake Ontario		Manitoba	Alberta
	Sibley	Ross't	Wawa*	Turkey	S.Bay'	Sarnia*	Pelee	L.Point*	NTOL	Wolfe I.*	McCreary	Suffield
a-BHC	11.	16.	14.	9.0	4.0	7.7	7.2	11.	19.	9.9	10.	16.7
Lindane	6.4	5.1	4.6	3.8	4.0	3.9	5.4	7.0	10.	6.9	5.2	5.2
Hept.Ep.	0.00	0.13		0.15	0.07	0.03	0.10	0.17	0.14	tr	0.02	0.04
Chlordane		0.05	0.02	0.03	0.00	0.04	0.06	0.06	0.11	0.14		
Dieldrin	0.00	0.13				0.32	0.42	0.49	0.14		0.05	
Endrin				0.04				0.00				
pp'-DDE	0.01	0.02	0.01	0.03	0.17	0.15	0.04	0.37	0.70	0.09	0.01	0.04
pp'-DDD							0.04	0.10		0.04		
pp'-DDT								0.04	2.1			
Methoxych.	0.57	0.69			0.58	0.96	1.4	3.1		2.1	0.13	0.19
PCBs	1.0	0.43	0.68	1.5	0.11	tr	0.94	0.24	3.7	0.46	1.3	0.02
HCB	0.02	0.02	0.04	0.03	0.04	0.40	0.03	0.07	0.03	0.01	0.02	0.06
Endosulf.	0.76	0.70	0.25	1.1	0.21	2.1	2.4	6.2	14.	3.0	1.6	2.9
Indene	0.77	10.	0.69	0.37	1.1	1.2	0.65	0.76	0.63	0.03	11.	0.00
1234-THN		18.		0.96							23.	
2-Me-NAP	19.	9.2	7.3	2.1		3.0	2.3	2.0	5.7	4.2	9.4	7.2
Quinoline	1.0	3.3	1.7			5.2	3.0	4.1	1.4	7.1		
1-Me-NAP	3.2	4.3	0.64		7.0	5.2	5.1	3.0	7.0	12.	9.5	4.0
B-Cl-NAP	5.0										4.0	
Acenaphth.						1.5			2.5			
Fluorene						1.5	1.0		2.7			
Phenanth.		2.5				2.9	3.0	6.0	6.2			
F'anthene		2.4				4.7	4.2	6.6	6.0	3.9		
Pyrene		4.3				2.4	2.2	6.4	1.0			
meta-DCB			0.10	0.36	1.7							0.70
para-DCB		32.		0.00	3.6				1.3			
ortho-DCB			0.00							0.01		
135-TCB								0.01	0.01			0.02
124-TCB		0.07	0.03	0.05	0.22	0.09	0.06	0.13	0.00	0.01	0.05	0.15
123-TCB		0.04		0.02		tr	0.04	0.05	0.02			
1234-TeCB				0.01	0.06	tr		0.01	0.02			0.03
penta-CB		0.01		tr	0.02	0.03	0.01	0.02	0.01			0.03
Rain (L)	59.5	67.7	85.0	123.7	36.6	61.7	71.1	56.0	56.9	54.7	59.1	50.9

* analyses incomplete on these stations - additional samples

Mass Transfer Coefficients (Vapor Exchange)

A start was made in determining the bulk mass transfer coefficients of persistent organic chemicals. A review was completed on methods of predicting these coefficients.

Little Turkey Lake System

Little Turkey Lake is a small (19 ha) lake with only a single inlet of consequence and only one outlet. Its bathymetry is regular and there is an existing body of data on flows and water chemistry. A number of preliminary samples were collected for water (centrifuged), suspended load, sediment and some leaf and ground cover.

Modelling the Role of Atmospheric Organic Chemicals

The fiscal year 1986/87 saw several important meetings aimed at determining the significance of the atmosphere in the toxic chemical budgets of the Great Lakes. The most significant was the International Joint Commission's Workshop on the Estimation of Critical Pollutants Atmospheric Loadings of Toxic Chemicals to the Great Lakes Basin. The background paper for this was prepared under this project and lively discussion ended by concluding that only PCBs and lead could provide an adequate data base for undertaking their mass balance accounting in each of the Great Lakes, including the role of these substances in the atmosphere. In both of these cases, the atmosphere was seen as the major input to the system, although its role in the lower lakes was decreased, relative to other sources. Benzo(alpha)pyrene could also be modelled for Lake Superior, where it was also deemed to be mainly derived from the atmosphere. Other lakes could not be modelled, at least in part because of the absence of data for the connecting channels and often for other compartments as well. A comprehensive data set is needed for the compartments of aquatic-atmospheric systems to be used to validate such models.

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Effects of Climatic Change on Water Quality

L.D. Delorme, Study Leader

N.S. Harper
D.L. Holloway

L.D. Delorme

INTRODUCTION

This study was started in 1984 as part of a program that was and continues to be funded in part by the Canadian Climate Program (CCP). One of the objectives of this program is the prediction and monitoring of longer-term climatic variability and changes in Canada. In order to accomplish this task, it is necessary to understand the water climate cycle and the geological history of climate change. This will be attempted by the development of climatic proxy data.

Geographically the area to be studied was the Canadian prairie. This area was chosen because the climatic records are short and longer records are required to prepare drought scenarios. To this end, 22 lacustrine sediment cores have been collected. The grid from which the cores were collected, is 3 degrees longitude, 1.5 degrees latitude. Not all cores will provide useful information.

Climatic proxy data is obtained from fossil shelled invertebrates called ostracodes. A complete data base of physical, chemical and meteorological data is available for Canadian freshwater ostracodes. Ostracodes exist in most lakes, ponds and streams; thus they are suitable organisms for deciphering past lacustrine and climatic conditions. The ostracodes are controlled in their habitats by a number of factors, one of these being alkalinity. Salinity of lake or pond water is in turn controlled by atmospheric precipitation, temperature and source of chemical ions. Climate is considered to be the driving force for the variability seen in the chemistry of small lakes and ponds.

One of the major thrusts of this study is the development of a suitable paleoenvironmental predictive model. The model will be used to interpret the paleoclimate of the past several hundred years.

Time or chronology is another important component of this study. With the use of palynology, we are in the process of delineating the rise and fall of *Salsola* fossil pollen (Russian thistle). This is an introduced plant to North America. It thrives during dry periods, consequently there is a dramatic rise in fossil pollen during these periods. Pb^{210} dating assists in establishing the specific data for the rise and fall of *Salsola* pollen. C^{14} dating is used to date the older sediments.

RESEARCH RESULTS

The point of change method (Esterby and El-Shaarawi, 1981) has been used on the absolute counts of *Salsola* fossil pollen to determine when the plant invaded the Canadian prairie. A preliminary date, of when this event took place is around 1925. The rise of *Salsola* fossil pollen has been shown in three of four cores in Saskatchewan (Fig. 29). The fourth core was from north-central Saskatchewan, where there was no invasion by Russian thistle.

The proof of how well an interpretive model is working is to correlate the interpreted values with observed values. This has been attempted for a core from Clearwater Lake, Saskatchewan. Based on the number of years of observed mean annual temperature data, the correlation coefficient is 0.6 (Fig. 30) for annual precipitation and 0.7 (Fig. 31) for mean annual temperature.

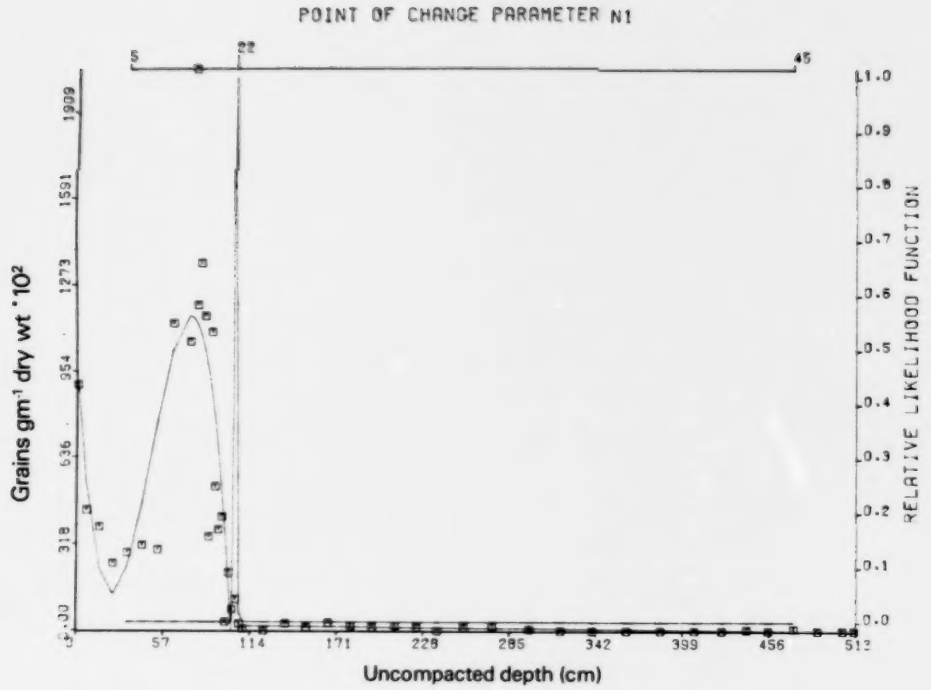

Figure 29. *Salsola* **sp. point of change at an uncompacted depth of 106.2 cm (1924 AD) for the Clearwater Lake core, Saskatchewan.**

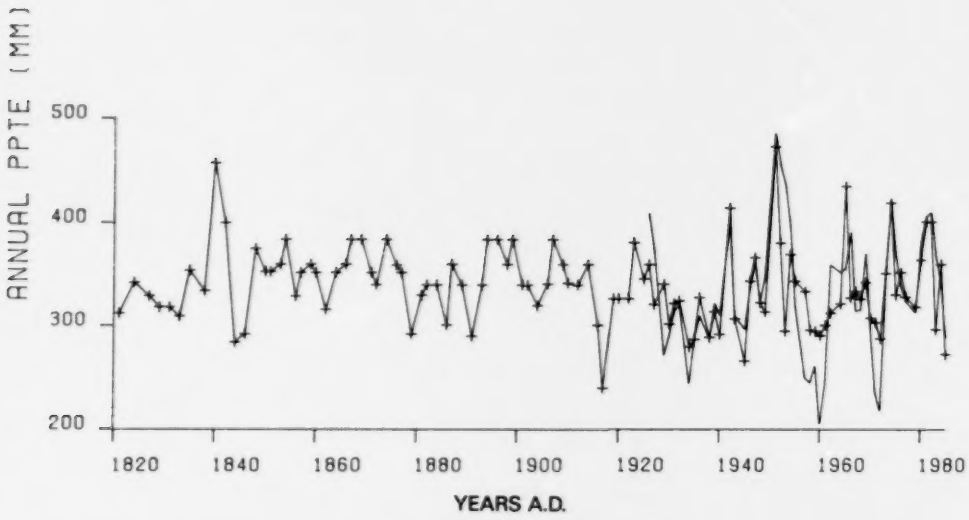

Figure 30. Correlation (r = 0.6) between interpreted annual precipitation based on fossil ostracodes from the Clearwater Lake core and observed mean annual temperature from Beechy, Saskatchewan. Line with symbols interpreted, other from observed data.

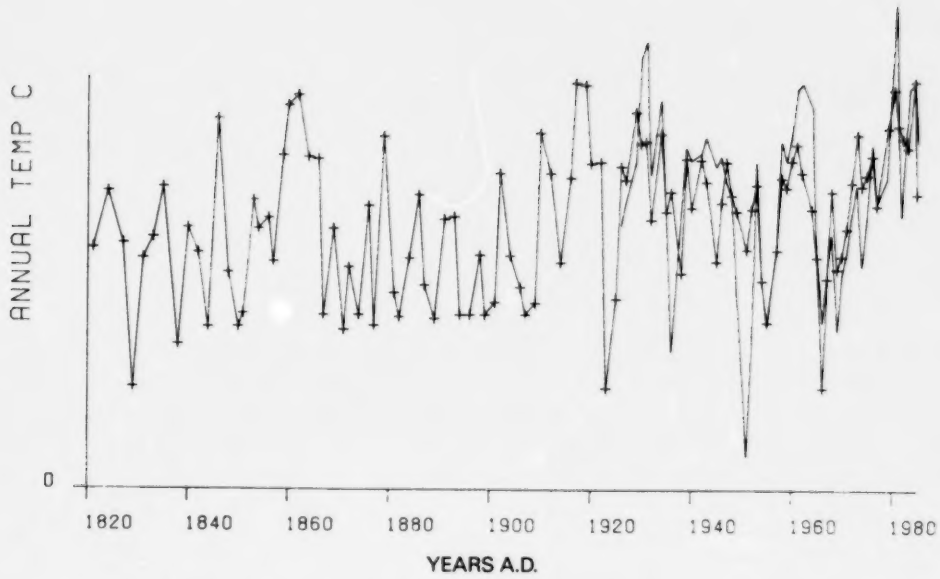

Figure 31. Correlation (r = 0.7) between interpreted mean annual temperature based on fossil ostracodes from the Clearwater Lake core and observed mean annual temperature from Beechy, Saskatchewan. Lines with symbols interpreted, other from observed data.

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Freshwater Ostracoda and paleoenvironmental interpretations from the Vermillion Lake site (Core 119), Alberta.

Freshwater Ostracoda and paleoenvironmental interpretations from the Horseman sites (Core 102), Saskatchewan.

Ostracoda from Lake Ontario and suspected Champlain Sea sediments.

Distribution of freshwater ostracodes from the tundra region of arctic Canada.

Summary of recent and fossil freshwater ostracodes of Canada.

Brackish and freshwater Ostracoda of a beach deposit from Dawson Bay, Lake Winnepegosis, Manitoba, Part 2.

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Aquatic Plants as Biomonitors of Atmospheric Deposition of Metals

W. A. Glooschenko, Study Leader

W.A. Glooschenko

INTRODUCTION

Concern with the long-range atmospheric transport of contaminants has led to the establishment of monitoring programs. In remote northern areas of North America and Europe, precipitation sampling networks have not been in operation until fairly recently, in particular because of the costs of installation and maintenance in isolated areas. In areas without precipitation sampling networks, other means of environmental monitoring have been used. These involve the use of plants which accumulate metals and lake sediments. Emphasis has been placed upon lower plants, especially mosses and lichens. Dead plant remains, i.e., peat and litter, also have been used. The choice of vegetation must be made to maximize the atmospheric input of metals and minimize the role of the substrate the plant grows on or in the case of higher vegetation, is rooted in. The ecosystem that fulfills this requirement is the bog, an ombrotrophic ecosystem receiving chemical inputs solely from atmospheric sources. Two major approaches have been used to delineate metal deposition: the use of living bog vegetation as a biological monitor of metal inputs and profiles of metals with depth in bog peat.

Two types of previous studies have taken place using bog vegetation and peats. One of these approaches is to determine the areal distribution of metals in mosses in areas of point sources. This has been done for Canadian smelters including Sudbury, Ontario, and Rouyn-Noranda, Quebec. A similar approach has been done in the iron-mining area of Atikokan, Ontario. Another type of study is to use metal concentrations in mosses to determine regional, background levels of atmospheric deposition. For both purposes, use has been made of the ombrotrophic moss species *Sphagnum fuscum*. This moss is ideal as it occurs all over Canada and northern Europe allowing inter-comparison of data.

RESEARCH RESULTS

During 1986/87, research consisted of a compilation of metal analysis data from previously collected samples across Canada. This included old, published data and new analyses from mosses collected the previous year mainly in the Prairie provinces. Other samples were from the Queen Charlotte Islands in British Columbia, the Northwest Territories, mid-Canada and the Atlantic coast, including Nova Scotia and Labrador.

Samples from 43 representative sites were chosen for analysis of 52 elements using NAA and DCP methods. Sites were mainly in remote boreal forest regions of the country. In addition, the mining/smelting centers of Thompson and Flin Flon, Manitoba; Atikokan and Sudbury, Ontario, and Rouyn-Noranda, Quebec were sampled. Emphasis was on the following trace metals: As, Bi, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sc, Sb, V and Zn.

Some elements were elevated in moss tissue in the vicinity of all the mining/smelter areas. These included As, Cd, Cu and Pb. Other elements were higher in concentration near a particular site. For example, mosses collected from Thompson, Manitoba, were high in V, Cr, Co and Ni, while Rouyn-Noranda samples were high in Bi, Cr, Co, Zn, Se, Mo and Sb. Of particular interest was Pb. This metal was relatively low in concentration in all western Canada sites and Labrador. It was higher in concentration in Ontario and Quebec samples apparently due to the proximity of the major population centers of eastern North America. Zinc also was high in most sites except on the west coast.

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Aquatic Partitioning of Radionuclides

R.F. Platford, Study Leader

S.R. Joshi
J.A. Fitzgerald
and S.P. Thompson

R.F. Platford

INTRODUCTION

This study is a continuation of the 1986 study "Aquatic partitioning of radionuclides." The objective is to obtain background activities of several low-level radionuclides in the Great Lakes Basin. We wish to determine their chemical speciation and their partitioning among the compartments: surface microlayer, water, suspended solids and sediments.

The radionuclides of interest are: H3, Cs137, Pb210, Po210, Rn222, Ra226, Th234, U234, 238, Pu238, 239, 240, and Am241.

RESEARCH RESULTS

We have found that the levels of some of the above-mentioned radionuclides in the top 100 μ of water can be 2x to 100x higher than in the subsurface water of lakes Ontario and St. Clair. Furthermore, activities in the foam which accumulates just downstream of Niagara Falls are 1000x higher than in the subsurface water, thus providing us with a convenient natural collector for what is probably atmospheric fallout.

In addition to the radioactivity from weapons testing, there is a significant contribution which has reached the lakes as a result of either uranium mining or by weathering of minerals. The uranium undergoes radioactive decay to give radioactive daughter products among which are the potentially hazardous Ra226 and Rn222.

From a knowledge of radionuclide concentrations in Lake Ontario, and of the chemical state of the water, we have prepared speciation diagrams of the various uranium decay products and of some transuranic elements in the lake. Some of the results are shown in Figure 32, with the redox potential and pH in the lake represented by the cross-hatched oval area.

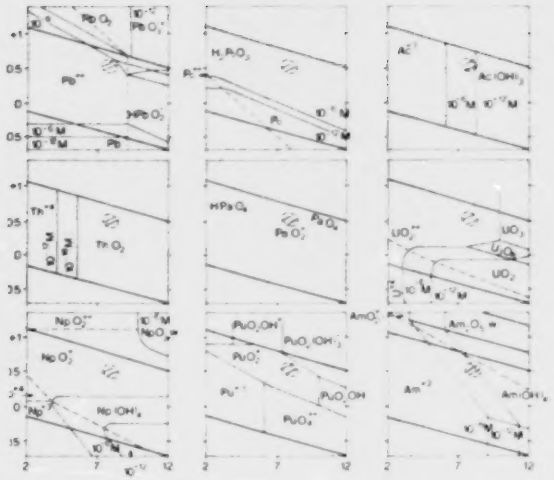

Figure 32. Stability diagrams for nine of the elements considered in lake water. The Eh is given in volts relative to the normal hydrogen electrode at 25°C. The effect of temperature in natural solutions is generally smaller than the uncertainty in the diagram fields.

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Climate Impact on the Physical Regime and Water Quality Responses of Lakes

W.M. Schertzer, Study Leader

T.J. Simons
W.M. Sawchuk
D.S. Munro
R.C. McCrimmon

W.M. Schertzer

INTRODUCTION

This study examines the effect of climate on the physical regime and water quality responses of lakes. The general objectives in the last three years were to develop a modelling format capable of analysing the climatic effects on the Lower Great Lakes for a climatological time frame. This required detailed specification of heat and water exchanges at the air-water interface, simulation of the thermal stratification cycle and application of water quality models to selected Great Lakes problems such as anoxia in the central basin of Lake Erie.

Analysis of the model results showed that lake evaporation is a critical component in the specification of the surface boundary condition and influences the magnitude of the energy flux at the air-water interface. Lake evaporation is also a key parameter in the variation of lake water levels and is an IJC reference.

RESEARCH RESULTS

Studies in the fiscal year 1986/87 utilized numerical models of the lake energy balance developed in the fiscal year 1985/86 to extend computations of the daily surface heat flux and components for Lake Erie and Lake Ontario over the climatological period 1953-1983. The model contains many improvements over previous research efforts. In particular, shortwave radiation fluxes are computed from a radiative transfer algorithm which explicitly treats multiple scattering effects. The model for longwave radiation explicitly treats clouds and aerosol effects. Turbulent heat fluxes explicitly incorporate atmospheric stability effects, while meteorological conditions above the lake surface are evaluated from scaling functions which transform meteorological data recorded at land stations at or near the lake perimeters to equivalent overlake data. Figure 33 provides a time series of computed lakewide heat storage based on the energy balance computations, and results compare well with measured heat storage. No long-term trend in annual heat storage values is evidenced despite the fact that air temperatures at nearby stations, e.g., Toronto and Rochester, show a consistent downward trend in annual temperatures over this period. Interannual variations can be considerable from year to year especially in Lake Erie.

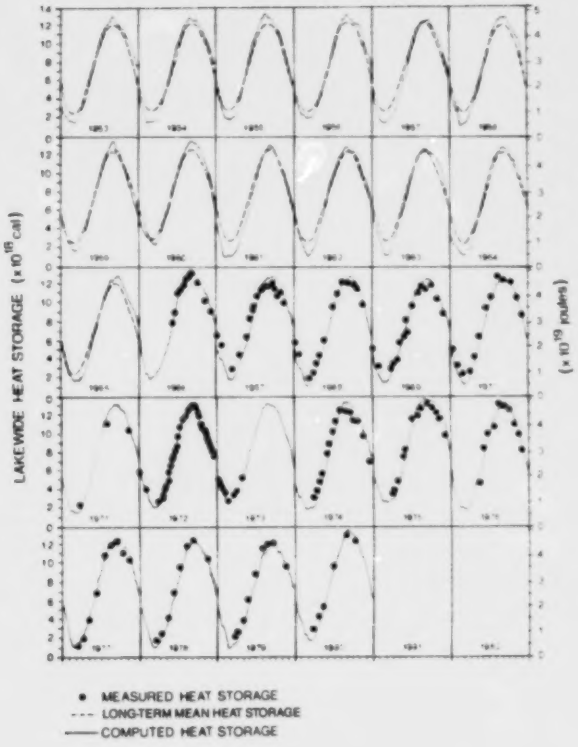

Figure 33. Comparison between observed and computed lakewide heat storage in Lake Ontario.

Additional studies in the fiscal year 1986/87 were conducted to augment the climatological modelling framework in the area of surface water temperature and ice extent. In this regard, a sophisticated numerical dynamic reservoir model DYRESM was applied to Lake Erie and Lake Ontario during 1967-1983 to provide improved estimates of these components suitable for inclusion in the primary energy balance model. Figure 34 provides an example of the surface water temperature simulation for Lake Ontario. Satisfactory results were derived from simulation of ice extent in both lakes. DYRESM was also applied in a feasibility study on Hamilton Harbour to simulate the seasonal vertical temperature structure.

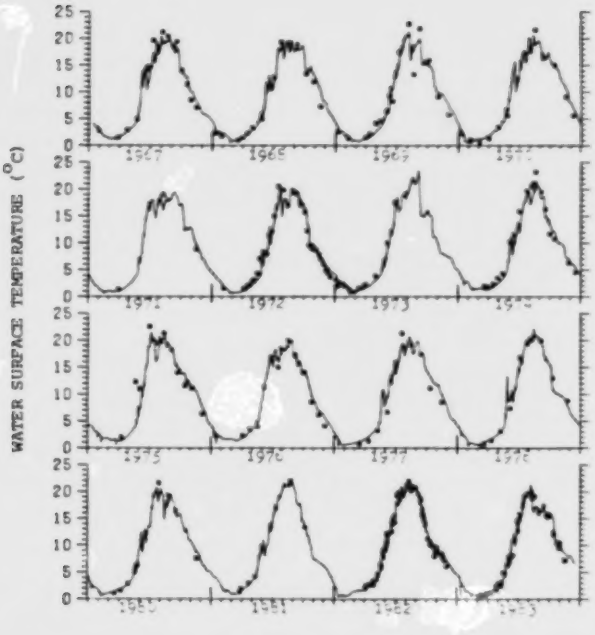

Figure 34. Time-series of Lake Ontario simulated and observed water surface temperature.

Research results from the energy balance models enabled verification of and application of one-dimensional vertical temperature models developed at NWRI to simulate the long-term seasonal stratification cycle for Lake Ontario. Figure 35 provides a summary of the thermal structure for the period 1953 to 1983 for Lake Ontario.

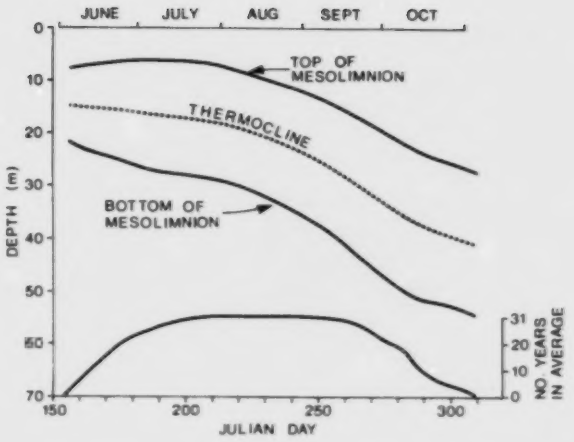

Figure 35. Long-term mean computed depth of the top and bottom of the mesolimnion and the thermocline position for Lake Ontario during the period 1953 to 1983.

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Nutrient/Contaminant Interactions

J.H. Carey, Project Chief

J.H. Carey

This project examines the relationship between lake trophic status (productivity, nutrient levels and biological structure) and contaminant dynamics (bioaccumulation, biodegradation and removal rates) and determines the factors controlling the vulnerability of a lake ecosystem to contaminant inputs. Research and management of the eutrophication and contaminants issues have historically been undertaken separately. The result of this separation of activities is that we lack the knowledge base to predict the effect that the implementation of remedial measures in our subject area will have on the other. For example, some recent evidence suggests that the availability of organic contaminants to lake biota, particularly at higher levels of food webs, may be inversely related to the biological productivity and thus the nutrient status of a lake. Continuing reductions in phosphorus loadings to the Great Lakes could serve unintentionally to maximize exposure of fish and other biota to contaminants already present in the system. In such cases it would be preferable to optimize lake trophic status so as to minimize contaminant impacts. Research to define the predictive relationships between nutrients and contaminants is clearly needed before improved (and possibly less expensive) management strategies can be developed.

In this project a multidisciplinary approach is employed which attempts to characterize and quantify the critical processes controlling the interaction of nutrients and contaminants in lakes. The research examines the general hypothesis that nutrients influence organic contaminant activity by influencing three critical processes: bioaccumulation (and subsequent effects), degradation and sedimentation.

Although much of the knowledge gained in this project will be applicable to many lakes, the major thrust of the project is to predict the influence of nutrient concentrations on contaminant fate, partitioning and transport rates in the Great Lakes. A comprehensive data set of contaminant distribution and effects will be compiled and evaluated for statistical significance. Initial emphasis will be on the system from Lake St. Clair to Lake Ontario and will include several IJC Areas of Concern, such as Hamilton Harbour.

It is anticipated that data from the Great Lakes will not span a large enough range of parameters, such as harness, trophic state, etc., to allow the determination of the controlling factors in contaminant distributions. Therefore, a series of headwater lakes, differing in limnology and devoid of point-source contaminant inputs will be examined. The partitioning of contaminants between water (soluble, colloidal and particulate phases), sedimenting material, sediments and biota, will be measured and related to nutrient loadings of the lakes.

Selected contaminants will also be added at sub-lethal levels to natural populations in large lake enclosures, augmented with different levels of nutrients. Bioaccumulation and degradation rates will be measured and related to nutrient loadings. The effects of dissolved and colloidal organic matter on biodegradation, photodegradation and sedimentation will also be examined. As a complement to the lake enclosure experiments, radioactive contaminants will be added to simple microcosms to determine the influence of nutrient and organic substrate on microbial biodegradation. The microcosms will permit experiments under more controlled and reproducible conditions than may be available in the field experiments and should provide insights into important processes needed to interpret the field results. Laboratory studies on the reductive transformations of contaminants will be conducted to determine the pathway of these transformations and the importance of such reactions in anoxic lake environments. A filter cascade procedure for isolating biota and colloids from lake water will also be designed and tested.

Processes Affecting Contaminants Distribution and Dynamics in Lakes and Estuaries

J.H. Carey, Study Leader

D.R.S. Lean
J.H. Hart
P.A. Coletta

INTRODUCTION

This study is a component of the NWRI Nutrient/Contaminant Interactions Project. It examines the dynamics of organic contaminants at selected field sites to determine the processes controlling contaminant distributions and pathways (bioaccumulation, degradation and removal rates). This information will be combined with the results of limnological investigations at these sites to examine the relationship between trophic status and contaminant dynamics. Field work is primarily focused on the Great Lakes ecosystem, both in the lower Great Lakes themselves and at headwater lakes which offer a greater range of trophic status and water quality and are devoid of point sources of contaminants. Contaminant pathways at other locations are also examined in support of other projects and operational groups. For example, in British Columbia, the aquatic pathways of chlorophenols used in the lumber industry are being studied in the Fraser River estuary. In addition, a site-specific contaminants list for the estuary for use by the agencies designing the water quality plan under the Fraser River Estuary Management Program (FREMP) is being formulated.

RESEARCH RESULTS

Nutrient/Contaminant Interactions

During the year, a preliminary survey was conducted at four lakes in the Bancroft, Ontario, area to determine if atmospheric inputs of contaminants were high enough to permit studies of compartmental dynamics. Samples of several species of fish, sediments, plankton and benthic biota were collected and prepared for contaminant analysis which is in progress. Preliminary results indicate that levels are lower than in the Great Lakes, as expected, but concentrations of several PCB congeners and other organochlorine compounds are high enough to allow more in-depth studies.

In collaboration with scientists from York and Waterloo universities, a survey of organochlorines in zooplankton from 28 lakes in northeastern Ontario was conducted. Although the analyses are not complete, preliminary results reveal several interesting features. PCB congener distributions in most of the lakes was strongly biased towards lower chlorinated isomers relative to the distribution observed in the Great Lakes. This observation is consistent with the presumed atmospheric source of these compounds and likely indicates the absence of point sources.

Absolute concentrations of these compounds correlated poorly with lipid content of the zooplankton, and since the lakes are all in the same area and likely receive similar atmospheric loadings, it seems likely that factors such as lake physics and limnology play a significant role in determining contaminant equilibria.

Fraser River Estuary

During the year, an identification survey was carried out to determine the identities of the major contaminants in several species of fish from the estuary. The major contaminants were found to be p, p'-DDE, alpha-chlordane, penta- and tetrachloro- anisoles, hexachlorobenzene and a number of cholorinated biphenyl isomers. The chlorobiphenyl isomer pattern indicated sources of Aroclor 1260 in both arms and a source of Aroclor 1254 in the North Arm. Further analyses are under way.

In the initial phase of this study, pentachlorophenol and 2,3,4,6-tetrachlorophenol were observed to be the most prominent chlorophenols in fish and water from the estuary. In addition, lower chlorinated congeners were present in some of the larger fish, but not in some of the smaller individuals of the same species. In an attempt to verify these observations, study scientists collaborated with Pacific and Yukon Water Quality Branch personnel in analyzing the relationship between age and the identity and concentration of chlorophenols in Fraser River starry flounder. WQB are involved in a multi-agency effort to develop a water quality plan and monitoring program for the estuary under FREMP and wished to evaluate the usefulness of starry flounder as a biomonitor. More than 90 starry flounder samples, from one to nine years of age, were collected, extracted and analyzed. The results to date do not show the age dependent isomer distribution previously observed and are in agreement with a simple dynamic equilibrium for all ages. A more complete picture will emerge when all analyses are completed.

During the year, as part of a collaborative investigation with NWRI physical limnologists into the transport dynamics of chlorophenols in this system, the river was sampled under high and low flow conditions. Under high flow conditions, water velocities of several knots were observed and the residence times of a 'plug' of water in the lower estuary, as measured with drogue markers, varied from three hours in the Main Arm to approximately ten hours in the North Arm. Saltwater intrusion into the estuary was minimal and turbidities were high. Under these conditions, chlorophenol inputs would be carried out into the Strait of Georgia with little degradation or deposition. Under low flow conditions, water velocities were substantially reduced and residence times in the lower estuary were of the order of days. Under these conditions, some photodegradation can occur at the surface, but overall residence times are still too low for substantial degradation to occur. Thus most of the chlorophenolic inputs are carried out of the estuary and the fate of these compounds is ultimately determined by factors in the Strait of Georgia.

Suspended sediment was sampled with a portable centrifuge and analyzed for a variety of contaminants. Contaminant levels were low; many compounds, including chlorophenols, were not detected. Since partitioning of organic contaminants to the sediment is dependent on carbon content and the carbon content of this sediment was only about 3%, this result is readily explained. These observations lead to the conclusion that unless the contaminant enters the system already absorbed on a high organic sediment (e.g., sewage sludge), sediment partitioning within the estuary will be unimportant and transport to the Straight of Georgia will occur primarily in the water phase.

Photodegradation Studies

The lampricide 3-trifiuoromethyl-4-nitrophenol (TFM) is used in the Great Lakes for control of the sea lamprey (*Petromyzon marinus*). Studies of the degradability of this compound indicated that it is very resistant to chemical reactions and biodegradation, but our laboratory studies into its photodegradation revealed that sunlight could degrade this compound into at least seven products. To confirm that this degradation was environmentally significant, we investigated a stream receiving an actual TFM treatment. Samples of water from upstream and immediately downstream of the treatment site were obtained. Further samples were collected over the next three days as the TFM 'plug' moved downstream. These samples were analyzed for TFM and its degradation products. As shown in Figure 36, most of the photoproducts previously observed in our laboratory studies of TFM photodegradation were observed in the treated stream three days after treatment. The results confirmed that photodegradation of TFM occurs under field conditions.

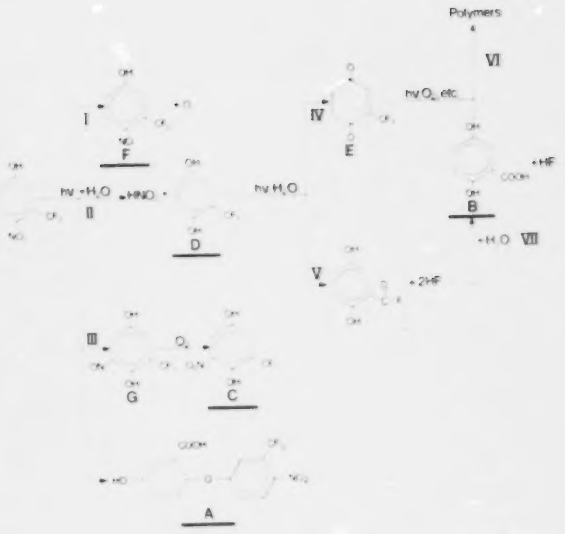

Figure 36. Pathway of TFM photodegradation with photoproducts observed in the current study underlined.

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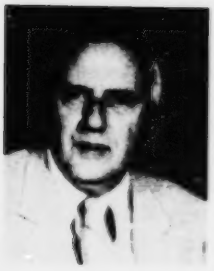
Reductive Dechlorination of Environmental Contaminants

R.M. Baxter, Study Leader



R.M. Baxter

INTRODUCTION

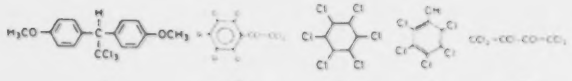
This is a part of a continuing study on the interactions between biochemical reactions and other chemical processes in the transformation of chlorinated organic contaminants. Previous investigations were concerned with biochemical oxidation and the subsequent transformation of the products by photolysis or spontaneous polymerization. Many important contaminants, however, are relatively resistent to oxidative processes, but readily undergo at least primary degradation under reducing conditions. Such reactions are of interest not only for the role they may play in the destruction of contaminants, but also because in certain cases the reduced product may be more toxic than the original material.

Reductive dechlorination (i.e., the replacement of an organically bound chlorine atom by a hydrogen atom) is one of the most important reductive processes which environmental contaminants may undergo. Work during 1986/87 dealt with one reaction of this type: the reaction between organochlorine compounds and reduced heme.

RESEARCH RESULTS

The procedure used was to incubate a mixture of the substance being tested, heme, and sodium dithionite (a reducing agent) in the presence of a surface-active agent, to maintain a homogenous suspension. At intervals, samples of the mixture were extracted with an organic solvent and the disappearance of the starting material or the appearance of product were followed by an analysis of the extract by gas chromatography. Appropriate control experiments were carried out to ensure that all components of the reaction mixture were necessary.

The structures of some reactive and non-reactive compounds are shown in Figure 37.



1 2 3 4 5

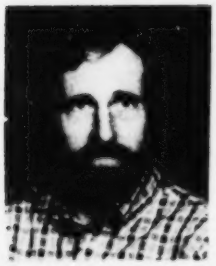
Figure 37. Methoxychlor (MOC,1) and octachlorostyrene (OCS,2) are similar in possessing both a chlorinated aromatic ring and a chlorinated aliphatic part, saturated in MOC and unsaturated in OCS. MOC reacts and OCS does not. Lindane (3) has a chlorinated alicyclic structure and pentachlorophenol (PCP,4) has a chlorinated aromatic structure. Lindane reacts and PCP does not. Hexachlorobutadiene (HCB,5) does not react, although other studies have shown that many other chlorinated alkanes do.

From these observations it appears that the reactivity depends on the electronic structure of the compound; compounds in which the bonds are delocalized by aromaticity (e.g., PCP), conjugation of an aliphatic structure (e.g., HCB) or both (e.g., OCS) do not undergo the reductive dechlorination reaction.

Report on 1979-1980 Intensive Surveillance Studies on Lake Erie: Special Issue of the *Journal of Great Lakes Research*

F.M. Boyce, Study Leader

M.N. Charlton



F.M. Boyce

INTRODUCTION

A field program of physical measurements, jointly undertaken by NWRI and the Great Lakes Environmental Research Laboratory (GLERL) (Ann Arbor) in 1979 and 1980 provided the core of a multidisciplinary study of Lake Erie (primarily the central basin) that extended the work begun in 1970 with Project Hypo. The scale of the effort was comparable to that of the International Field Year on Lake Ontario, but with somewhat less publicity. Rather than publish separately the individual results of the sub-studies, it was decided to produce a synthesis report in the form of a special issue of the *Journal of Great Lakes Research*. This report will be published as Number 4 of Volume 13 in late 1987 and will include 30 papers, 18 of them authored or coauthored by NWRI scientists. The editorial team comprises F. Boyce and M. Charlton from NWRI, C.H. Mortimer (University of Wisconsin), D. Rathke (Ohio State University), and J. Bennett (Environment Research Institute of Michigan). Lead responsibility was taken by F. Boyce.

RESEARCH RESULTS

The physical studies have lead to a clearer understanding of the large-scale circulation of the lake, in particular its sensitivity to the variations of wind stress across the basin. The dynamic role of small-scale features of thermal structure has been clearly documented. Efforts to comprehend the oxygen budget of the central basin's bottom waters make it clear that a better understanding of sediment water interactions is required. This will be a major thrust of any future work. The report documents a substantial advance of knowledge and its application through modelling.

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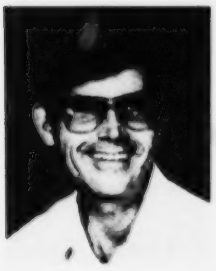
Influence of Trophic State on Toxic Contaminant Biodegradation Rates

B.K. Burnison, Study Leader

D.J. Nuttley
G. MacInnis



B.K. Burnison

INTRODUCTION

Research to define the predictive relationships between nutrients and contaminants is clearly needed before improved management strategies can be developed. In an effort to understand the influence of nutrient and organic substrates on biodegradation rates of toxic contaminants, microcosms have been constructed to permit experiments under relatively controlled and reproducible conditions. These microcosms will also be used to study the effects of toxic contaminants on bacterial and phytoplankton populations. During 1986/87 pentachlorophenol (PCP) was chosen as the model compound for the intial microcosm experiment because of its prevalence in Hamilton Harbour water. In 1987/88, hydrophobic chlorinated compounds such as hexachlorobenzene and octachlorostyrene will be used.

RESEARCH RESULTS

The first microcosm experiment was set up on October 27, 1986. Undisturbed Hamilton Harbour sediment cores were obtained using the box corer on board the CSS *Limnos*. The 15.24 cm core was taken using the lower part of the microcosm apparatus. The six cores were returned to the NWRI environment chamber and the upper part of the apparatus was attached. Ten litres of Hamilton Harbour water was slowly added to each microcosm. Filter sterilized lake water was added daily to each microcosm with a simultaneously withdrawal of an equal volume of microcosm water. After 10 days, phosphorus was added at two levels in two microcosms. Four weeks were allowed for the aquatic community to equilibrate to the new nutrient level. At that time a daily addition (equivalent to 5 μg/L) of phentachlorophenol (PCP) was added to all microcosms except a control. The biomass and activity of the algae and bacteria were monitored routinely by measuring chlorophyll, phytoplankton count, primary productivity (^{14}C, light and dark), direct bacterial count, bacterial production (^{3}H-thymidine method), bacterial heterotrophy, PCP decomposers (^{14}C-PCP MPN procedure), dissolved oxygen, PCP concentration, and water quality determinations. After seven weeks ^{14}C-PCP was added to all microcosms and the movement of the label was monitored in the dissolved and particulate fractions as well as the fraction isolated by hexane extraction of the whole water sample.

The preliminary results show the phytoplankton population increased greatly in the phosphorus-supplemented microcosms, but the higher nutrient level did not protect them from the toxic properties of PCP (or other toxic contaminants within the PCP preparation). Algal productivity and dissolved oxygen decreased sharply after PCP additions and bacterial activity increased (both via productivity measurements and by cell count). Many of the chemical determinations for water quality and PCP concentrations are not completed at this time. Nevertheless, it appears that even though the calculated PCP level reached 85 μg/L in the five microcosms the level of PCP was maintained at approximately 25 μg/L. Monitoring of the added ^{14}C-PCP indicated a decreasing amount of the radioactivity could be accounted for in the water column (100% down to 70% of the calculated total). Only 1% was in the particulate fraction and it is assumed that the increasing proportion went to the sediments. The tubifex worms had accumulated more than an equilibrium amount of isotope. Preliminary results indicate that daily additions of phosphate do not significantly increase the biodegradation rate of pentachlorophenol. However, we do not have the complete set of soluble reactive phosphorus (SRP) data for the microcosms to infer that phosphate was available to the decomposer population. The competition for phosphate was most likely very high considering the large algal biomass in the P-enriched microcosms. In future microcosm experiments with radioactive contaminants a means of routinely sampling the sediment must be included.

PUBLICATIONS

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Statistical Analysis of Environmental Data

S.R. Esterby, Study Leader

S.R. Esterby

INTRODUCTION

Statistical methodology which leads to effective study design and efficient extraction of information from data is of considerable importance to environmental sciences. Several topics are considered in this study and the results consist of conclusions from data analyses and method identification and development. Statistical methods for the analysis of multiple sequences and for paleoenviromental calibration functions are considered and are applied to data sets for the inference of past pH. Sources of variability in Great Lakes surveillance data are determined to aid in better sampling design. Statistical methods for studying the covariation of nutrients and contaminants are also considered.

RESEARCH RESULTS

A general algorithm for grouping sets of observations, such as multiple measurements on a sediment core or water depth profiles, has been formulated. Some of the assumptions of the pH-diatom calibration functions have been examined by the analysis of a published set of data, with the conclusion that broad limits on inferred pH may be unavoidable. Some Lake Ontario data have been analyzed in the ongoing assessment of the contribution of temporal and spatial sources of variability. The sampling and laboratory variability have been determined in the three-ship intercomparison on Lake Erie. Temporal and spatial models for nutrients have been tested and temporal models for contaminants proposed.

PUBLICATIONS

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Influence of Nutrients on the Fate of Organic Contaminants in Lake Ecosystems

D.R.S. Lean, Study Leader

J. Carey
S. Esterby
I. Gray

D.R.S. Lean

INTRODUCTION

Balancing human demands on the environment with the overall welfare of the biosphere is one of the greatest challenges facing society today. In lakes, the limits of use and abuse are set by the biogeochemical processes. The flow of energy through the food chain is determined by the influence of light and nutrients, phosphorus and nitrogen. This has been our main activity in the past, but recently we have concentrated on the effect of pesticides and other toxic organic chemicals (OCs) on nutrient cycling and community structure. Alternatively, nutrients and consequently lake productivity may profoundly alter the fate of OCs. These observations will be used to predict why some fish are contaminated in areas but not others.

RESEARCH RESULTS

Manuscripts relating nutrient kinetics with heterotrophic and autotrophic community dynamics and losses through zooplankton grazing and sedimentation in Lake Ontario have been completed (1–12) and related to similar processes in small lakes (13–18). These results identify the critical processes that could be altered by toxic materials. Experiments are in progress at Lake St. George that relate to conversion efficiencies and (plankton) particle size distribution.

To predict the fate of OCs data for the distribution in the sediments, fish, plankton, colloids and the dissolved phase are required. Existing literature was found to be unreliable, unavailable or not collected in a consistent way. A survey is partially completed in headwater lakes which vary in trophic state, hardness and depth. Such observations will be essential to determine the relative importance of "toxic rain."

Rates of uptake of nitrogenous compounds were measured in acid-stressed lakes, other shield lakes, hard-water lakes and lakes where nitrate is elevated (Ontario) and where all nitrogenous forms are elevated (Hamilton Harbour). Furthermore, rates of assimilation of nitrate and sulfate in acid-stressed lakes have been measured and compared to similar lakes of neutral pH. The net assimilation results in the release of OH^- ions and in part neutralizing the effect of the acidity associated with atmospheric deposition of sulfuric and nitric acid. At the same time the relatively neglected process of nitrification (conversion of NH_4^+ to NO_2^- and NO_3^-) was investigated.

Experiments are currently under way to evaluate the influence of pesticides on phytoplankton and zooplankton in lake waters. The assimilation rate and subcellular distribution of ^{14}C-bicarbonate by phytoplankton into low molecular weight compounds, carbohydrate, protein and lipids provide insights into the metabolic effects of the pesticide on the entire phytoplankton community. The phytoplankton containing the recently produced photosynthate was fed to zooplankton (*Daphnia* sp.) and the activity of getting and assimilating food determined at various concentrations. It is shown that pesticides which influence neuro-muscular function had effects at sublethal levels and in some cases altered the ability to assimilate certain subcellular components.

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Speciation of Selected Pollutants by Organic Colloids In Surface Waters

G.G. Leppard, Study Leader

J. Buffle (University of Geneva)

G.G. Leppard

INTRODUCTION

This study attempts to characterize, and eventually to quantify, some coagulation processes which modulate the interactions and speciation of nutrients, organics and contaminants in lakes. A filtration cascade technology for isolating colloidal materials from lake water in an unperturbed or native state was developed in the preceding year. The purpose of this new technology development is to derive materials for quantitative testing of the properties of native colloids, such as fibrils, humics and amorphous iron. This in turn is expected to lead to an assessment of such colloids for their roles in sequestration and sedimentation processes which affect contaminant dispersion. Currently a focus is being placed on some colloidal forms of dissolved organic carbon (DOC) and phosphate and a certain filtration artifact (surface-induced coagulation/polymerization) which led in the past to misleading perceptions of their nature and of their capacity to respeciate soluble substances.

RESEARCH RESULTS

The principal results are:

1. the first description, at 0.003 μm resolution, of colloidal amorphous iron phosphate by high-resolution transmission electron microscopy in conjunction with energy-dispersive spectroscopy on a *per particle* basis;

2. a demonstration that filtration flow rate can be the major determinant of coagulation artifact within filter fractionation schemes employing filters whose pore sizes are 0.45 μm or less;

3. a demonstration that respeciation of at least three nutrients within a cascade filtration scheme is a function of filter-induced coagulation.

These results have the following significance for limnological studies on the properties of natural suspended particulates in the colloidal size range (0.001 to 1.0 μm least diameter), particularly suspected colloidal carriers of nutrients and/or pollutants.

The use of filter cascades for sizing amorphous iron phosphate colloids overestimates their diameter by one to two orders of magnitude and causes them to be incorrectly classified in the standard assessment of particulate vs. soluble species. Our demonstration of this is a first.

The use of energy-dispersive spectroscopy at high resolution on a *per particle* basis allows one to speciate the various iron phosphate colloids within a given sample on the basis of both morphology and relative molar ratios of iron to phosphate. Our demonstration of this is also a first.

Amorphous iron phosphate colloids are shown to sequester nutrients and to aggregate with large biotic sedimenting particles.

The use of filter cascades for fractionating lake water rich in fulvic acids is shown to result in coagulation phenomena whereby organic particles in the range of 0.003 to 0.010 μm are converted into aggregates of approximately 0.650 μm diameter. The release of or occlusion of nutrients/contaminants during this filter-induced coagulation is now open to systematic inquiry.

Through controlled manipulation of the filtration flow rate, we can now illustrate how DOC-rich or iron-rich lake water will fractionate in unanticipated ways to yield fractions bearing little relationship to what was intended. We can do this without using exaggerated conditions, and in some instances we are able to infer and test the mechanism behind the unanticipated redistribution of colloids. The study has advanced far enough that corrective measures can be designed into our cascade schemes.

At least for two lake water types (fulvic acid-rich, amorphous iron-rich), we can state that one can know the particulate constitution of one's fractions only by a microscopical examination of the fractions; inferences made from a knowledge of filter pore sizes are likely to be false. In turn, without a microscopical analysis, inferences made about contaminant speciation vis-à-vis particle size are also likely to be false.

We have further developed the systematic scheme for monitoring fractions by transmission electron microscopy initially developed at NWRI by Burnison and Leppard (1983). It is now simpler and faster.

PUBLICATIONS

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Sediment-Water Interactions

A. Mudroch, Project Chief

A. Mudroch

The overall objective of the project is to develop a thorough understanding of all biological, geochemical, sedimentological, and physical processes involved in lake sediment-water interactions. These processes, which define pathways, availability and release of contaminants in lake sediments, are presently the highest priority.

The bulk of persistant-hydrophobic toxic organic chemicals, heavy metals, radionuclides, and nutrient (phosphorus) contaminants in lakes are associated with bottom sediments. Thus a complete understanding of the sources, distribution, transport, redistribution and burial rates of sediments is critical to predicting contaminant fate and effects. Sediment processes such as resuspension, transport and erosion rates are studied, and sedimentation rates are measured to establish the geochronology of contaminant discharges to lakes. The geotechnical properties of fine-grained sediments are examined and sediment budgets for study ecosystems are developed. Samples of surficial sediments, sediment cores and suspended sediments collected in sediment traps, on filters, or by centrifugation are used to quantify these processes.

The measurement of contaminant release from sediments, and the effects of benthic organisms on these release rates are studied by performing microcosm level research in the laboratory and in the Great Lakes Areas of Concern such as Hamilton Harbour, the Upper Great Lakes Connecting Channels, the Bay of Quinte and others. The contaminants studied include the organics (dibenzo-p-dioxins, dibenzofurans, chlorobenzenes, PCBs, PAHs, organochlorine pesticides), the toxic metals (lead, cadmium, mercury, arsenic) and the radionuclides. Major elements, conservative tracers and particle size analyses are conducted to see whether behavior of contaminants can be correlated to these parameters. The toxic effects of in-place polluted sediments are addressed by population/community structure field studies in Areas of Concern, and by controlled exposure experiments in the laboratory. The bioavailability of sediment-associated chemicals is estimated by measuring the partitioning of chemicals between bottom sediments/pore water, suspended sediments/lakewater, and bottom and suspended sediments/biota.

Effects of Physico-Chemical Properties of Lake Sediments on Toxic Metal Distribution and Bioavailability

A. Mudroch, Study Leader

J. Metcalfe
S.S. Rao
S.R. Joshi

INTRODUCTION

Many metals originating from human activities and released into the aquatic environment become associated with sediments. The investigation of pathways of sediment-associated metals is important to quantify their release or accumulation by biota in a lake. In addition, metals may affect the community structure of sediment biota.

Recent studies have shown input of zinc and arsenic from gold mining activities into Yellowknife Bay of the Great Slave Lake in the Northwest Territories, and mercury and arsenic from past gold mining activities into the Shubenacadie River headwater lakes in Nova Scotia. A survey of distribution of metals in Lac St-Louis (St. Lawrence River) showed accumulation of metals in areas with fine-grained sediment deposition.

Historical trends of input of zinc and arsenic were investigated by the determination of age profiles of the sediment from Yellowknife Bay, Northwest Territories. Over the past three years, zoobenthos was collected to assess the bioavailability of sediment-associated mercury and arsenic in the Shubenacadie River headwater lakes. Surface sediment samples from Lac St-Louis were examined for various microbial physiological types and densities. A relationship was investigated between these organisms and concentrations of metals and nutrients in the sediments.

RESEARCH RESULTS

Concentrations of zinc and arsenic were determined in sediment cores collected at the depositional areas of Yellowknife Bay. Sedimentation rates were estimated using two different radiometric approaches: the depth profiles of Cs-137 and Pb-210. Geochemical composition of the sediment core indicated input of similar material into sampling areas over the past 50 years. Age profiles of the sediment constructed from the radionuclides measurements and concentration profiles of arsenic and zinc indicated the efficiency of implemented remedial actions at the gold mine.

Two species of mussels, *Anodonta implicata* and *Elliptio complanata* were collected from the nearshore zone of the Shubenacadie River headwater lakes. Mercury and arsenic were determined in the soft parts of the mussels. The concentration of mercury in *A. implicata* varied by a factor of 3 (0.5-1.5 μg/g) despite a wide range in the sizes (0.04-3.45 g) and ages (4-9 years) of the specimens. On the other hand, mercury concentrations in *E. complanata* varied by a factor of 17 (0.59–9.55 μg/g). Much of the variability was due to the size of the organisms. Tissue concentrations increased almost exponentially with increasing dry weight over a weight range of 1.0–3.0 g, suggesting that this species continually accumulates mercury as it grows. The age of specimens ranged from 5 to 17 years. However, the concentration of arsenic was similar in both species and did not vary with the size (dry weight) of the mussels.

Sediments from Lac St-Louis exhibited zones of high and low bacterial density. Low density zones were associated with higher concentrations of trace elements (nickel, cobalt, chromium, vanadium, copper, lead, zinc, and arsenic) in the sediment. In these zones, a greater quantity of free trace elements ions was elutriated from the sediment by distilled water which suggests they were in an available form. However, higher concentrations of trace elements had no apparent effect on the growth of ammonifiers and sulfur oxidizing bacteria.

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Erosion and Transportation of Contaminated Fine Sediments

J.P. Coakley, Study Leader

N.A Rukavina
A. Mudroch

J.P. Coakley

INTRODUCTION

Fine-grained sediments make up the bulk of the sediment entering the Great Lakes ecosystem. They are contaminated to a greater or lesser degree depending on their source. The most important sources of contaminated sediments are discharges from polluted rivers, erosion of polluted shoreline materials, dumping of polluted dredged spoils, and the resuspension of polluted bottom sediments.

Other fine-sediment sources are virtually uncontaminated and act to dilute the above inputs. These sources are composed primarily of erosion debris from the widespread glacial clays and silts that form the shoreline and nearshore slope. The ability to predict the rates of supply of such sediments is important not only for determining contamination loading and budgets, but also because it allows us to model the physical evolution of lakes created in such cohesive materials. Simply stated, we would then be able to address the question, How far will the developing shoreline recede before it finally reaches equilibrium with the lake level? In relatively young bodies of water such as the Great Lakes, and especially in reservoirs, answering this question is crucial to lake level regulation decisions and to setting reasonable guidelines for safe long-term shoreline development. Work to date has focused on the nearshore zone of Lake Ontario near Stoney Creek.

In a companion study, the transport of fine, often contaminated, sediments from known point sources is being investigated using tracer techniques. The test area is in the Toronto waterfront, an identified Area of Concern for Great Lakes water quality. The focus is on two sources of contaminated sediments: the Humber River and the Eastern Headland (Leslie Street Spit). Because contaminated fine sediments from these sources may be transported to nearby sensitive areas such as bathing beaches and drinking water intakes, it is important for environment management reasons that the transport pathways and trajectories of such sediments from known sources be defined as well as possible.

RESEARCH RESULTS

Contamination Hazard from Eroding Waste Disposal Sites

Of the 3300 listed waste disposal sites in Ontario, more than 230 are located within 5 km of the shoreline of the Lower Great Lakes; 60 are within 1 km of the shore. The hazard to lake water quality posed by erosion of these sites was examined from the point of view of physical destruction of the sites by the receding shoreline and the effect of groundwater discharges into the nearby lakes. Three sites were identified as vulnerable to shore erosion, while 31 sites could pose contamination hazards insofar as groundwater effects were concerned.

Literature Report on Tracing Fine Sediments

The report (now in final stages of preparation) catalogs and reviews over 100 references on this subject and evaluates their utility for the Toronto area study. Potential tracers of fine-sediment transport are classified into a number of types, e.g., artifical, natural, incidentally introduced, on the basis of their nature and method of preparation and analysis. The report concludes by outlining the selection of the most attractive tracer options.

Sediment Tracer Testing in the Toronto Area

Grab samples of surface sediment were collected over a dense grid in Humber Bay and off the Eastern Beaches in the Toronto waterfront in 1985 and 1986. Chemical analysis for background levels of selected trace metals has been carried out to identify possible incidentally introduced elements, such as lead and copper that may be used as sediment tracers. Neutron activation analysis for background cesium levels in the study area (of importance for future artificial tracer studies) showed favorably low and uniform levels (less than 3 ppm). In addition, investigations continue into the use of naturally occurring sediment properties, such as grain size distributions and anthropogenic particles, as sediment tracers as well.

The artificial sediment tracer selected for the first tracer study is a non-toxic ore of the element cesium. The tracer has been ground to silt size to simulate the hydraulic behavior of this size fraction. Initial injection was made in April 1987 at the mouth of the Humber River, with periodic sampling to continue up to December 1987.

Stoney Creek Field Site

In 1986, an attempt was made at a first-order model for predicting subaqueous erosion from wave-derived shear stresses, using hindcast wave data. The preliminary results were presented at the NRCC ACROSES-sponsored Symposium on Cohesive Shores (Coakley *et al.,* 1986). The predicted erosion rates, however, were an order of magnitude larger than those measured in the field. This suggested to us that the hindcast wave data used for the shear-stress calculations overestimated wave-induced shear stresses, or that other factors, such as intermittent sand cover of the till, were acting to retard or attenuate the effects of shear stresses.

The field study was continued in 1986. T-frames were reinstalled at the Stoney Creek site in mid-April and 12 sets of fixed-transducer readings and 5 sets of diver-control measurements were taken between April and December. Only minor decreases in elevation (erosion) occurred at the two sites with exposed till. Net change since measurements began in 1984 is still less than 2 cm, the precision of the procedure. Because of the low rate of erosion, monitoring in 1987/88 will be reduced to three sets of measurements by divers and will be based on direct measurement of depth-of-disturbance rods rather than acoustic data.

An updated wave measuring system was installed at the site for the 1986 field season. These data are now being analyzed and will be combined with the 1984 data to provide a more accurate picture of the wave climate at the site.

Literature Review of Shoreline Evolution in Reservoirs

A computerized search of references concerning shoreline erosion and related processes in reservoirs was conducted.

PUBLICATIONS

Coakley, J.P., Rukavina, N.A. and Zeman, A.J. 1986. Wave-induced shear stress and subaqueous erosion of cohesive tills. Proc. Symposium on Cohesive Shores, NRCC ACROSES 120-136.

Coakley, J.P. 1986. Contamination hazard from waste disposal sites near receding Great Lakes shorelines. NWRI Contribution 86-112.

Sedimentary Transport of Radionuclides in the Great Lakes with Special Reference to Lake Ontario

S.R. Joshi, Study Leader

S.P. Thompson
J.A. FitzGerald
A. Mudroch

S.R. Joshi

INTRODUCTION

During 1986/87, studies were initiated to investigate the influence of radionuclides derived from the Chalk River Nuclear Laboratories (CRNL) on the waters of the St. Lawrence River and to examine the sedimentary partitioning of radionuclides reaching Lake Ontario via the Niagara River. The nuclear reactor accident at Chernobyl in April 1986 prompted us to study the impact of the radioactive emission on the Canadian aquatic environment.

RESEARCH RESULTS

The results from these three investigations show that (i) very low levels of CRNL-derived radionuclides are detected in the Ottawa River, which subsequently joins the St. Lawrence River, (ii) the radionuclides inventory at one sediment core location in Lake Ontario reveals unusual pattern of deposition, and (iii) the Chernobyl emission had a negligible effect on the aquatic environment.

Results from a typical survey of radionuclides in the Ottawa River water are presented in Table 2. The data clearly show that very low, but detectable, amounts of CRNL derived radionuclides are present in raw, finished and centrifuged water samples. The data also show that although several radionuclides are obviously retained on the water filtration plant floc, radiologically more toxic Sr-90 is likely to provide a major dose to the population in the event of an accidental discharge. The results also suggest that many of these radionuclides are associated with the particulate fraction.

Table 2. Radionuclides in Ottawa River Waters—1986

	Level (mBq/L)		
Radionuclide	Raw Water	Finished Water	Centrifuged Water
Sr-90	18.4±0.4	17.4±0.4	17.0±0.4
Cs-137	3.5±0.5	0.9±0.4	3.7±0.5
Ce-144	3.2±1.0	ND	3.0±0.9
Co-60	0.5±0.2	0.4±0.2	0.7±0.2
Nb-95	82±39	ND	40±27
Mn-54	1.4±0.6	ND	0.6
Ag-110m	0.4±0.3	ND	0.4±0.2
Zn-65	ND	2.2±1.3	0.9

ND — not detected

Results from radionuclide inventory calculations for five stations in Lake Ontario are shown in Table 3. The data show that the total Cs-137 at station 210 (in the Niagara Sedimentary Basin) is significantly lower than at other locations. Americium-241 also follows the same pattern, while the plutoniums at this location are present at levels found at other sites. Clearly the nature of the associated materials exerts considerable influence on the subsequent deposition and burial of radionuclides.

Table 3. Radionuclide Inventories in Lake Ontario Sediment Cores

	MBq/km^2			
Station	Pu-238	Pu-239, 240	Am-241	Cs-137
206	3.0	116.9	42.9	6408
207	9.2	163.2	84.0	14486
208	16.3	135.4	56.6	16924
209	10.0	161.0	85.5	18245
210	7.8	131.0	3.3	660

The results from measurements on rain, snow and water filtration plant floc samples revealed that the Chernobyl radioactive emission had a negligible effect on the Canadian aquatic systems. Typical measurements on Burlington rain samples are shown in Figure 38.

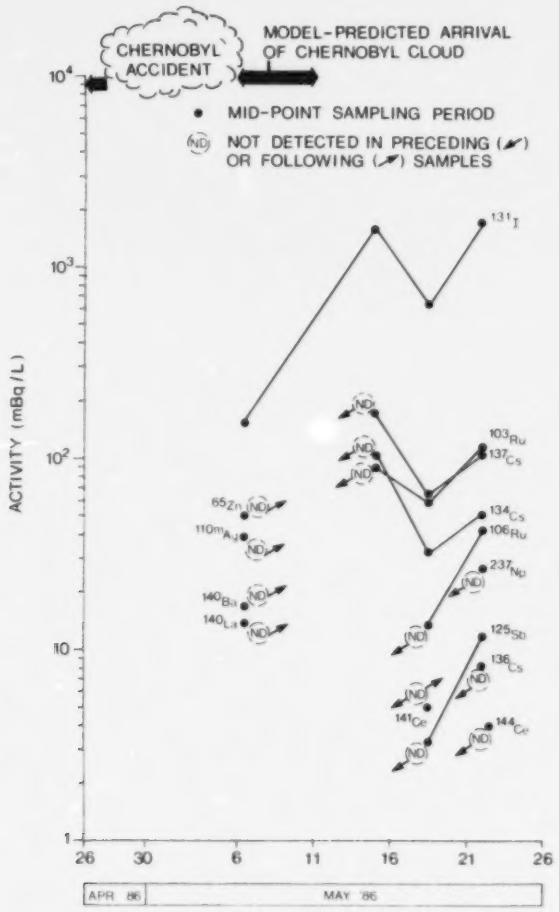


Figure 38. Measured levels of gamma-emitting radionuclides in Burlington rains (6-24 May, 1986).

PUBLICATIONS

Platford, R.F. and Joshi, S.R. 1986. The chemistry of uranium and related radionuclides in Lake Ontario waters. J. Radioanal. Nucl. Chem., Lett. 106: 333–343.

Joshi, S.R. 1987. Nuclear spectrometric determination of uranium isotopes without use of radiochemical yield monitors. Nucl. Instrum. Methods. A254: 349-354.

Joshi, S.I. 1987. Early Canadian results on the long-range transport of Chernobyl radioactivity. Sci. Total Environ. 63: 125-137.

Polynuclear Aromatic Hydrocarbons in Freshwater Environments

E. Nagy, Study Leader

J.H. Carey
J.H. Hart

E. Nagy

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are produced by combustion of various fuels, such as coal in energy production, wood in space heating, petroleum fuels in the internal combustion engine, and some industrial processes. As airborne pollutants, they may be widely distributed before deposition on land or water. Rivers may collect land-deposited PAHs from their drainage areas and accumulate them in lakes or offshore depositional zones. Additional PAH sources include municipal and industrial discharges into freshwater systems.

PAHs in freshwater sediments are considered significant pollutants due to their carcinogenic or mutagenic properties. In some areas of elevated concentrations, PAHs have been associated with fish tumors observed in the same areas.

The study was designed to develop a PAH data base for diverse geographic areas in Canada, to identify areas of high concentrations, and to relate PAH compositions (profiles) to possible sources in each area. In areas of specific concern, follow-up work will endeavor to study the movement, accumulation and persistence of PAHs in freshwater systems, especially sediments.

RESEARCH RESULTS

PAHs in St. Clair River sediments in the Sarnia area appeared to be related to industrial activity on the Canadian side of the river. PAH compositions were dominated by the low molecular weight, two- or three-ring polycyclic aromatics. The large number of methyl-substituted PAHs indicated a petrochemical, rather than combustion, origin of these compounds. The absence of odd-carbon predominance in the normal alkane fraction was a further indication of anthropogenic sources of sediment organics. The distribution of the two classes of organics in the river bottom showed the highly localized inputs, currents, and sediment characteristics.

PAHs in MacKenzie River suspended sediments were present at low concentrations, and were probably related to Norman Wells area oil seeps in a September 1985 survey. A second survey in June, 1986, however, found these compounds at measurable concentrations all along the river, overwhelming any input from the natural seeps or the Norman Wells refinery. These elevated concentrations were ascribed to a diffuse input by spring runoff from the river's drainage area. The normal alkane fraction of the organics exhibited some odd-carbon predominance (of C_{15} and C_{17}) indicating a degree of biogenic origin for these hydrocarbons in both surveys.

Analysis of sediment samples from Thunder Bay, Hamilton, and Toronto harbors, the St. Mary's River, and Lake Erie, showed several areas of high PAH concentrations, predominantly related to local sources. Analysis of selected sediment cores from the St. Lawrence River indicated highly localized historical inputs of PAHs in these sediments.

PUBLICATIONS

Nagy, E., Painter, D.S., and Scott, B.F. 1986. Fate and impact of 2,4-D in a pond ecosystem. Proc. 1st Int. Symp. on Watermilfoil and Related Haloragaceae Species. Vancouver, July 23-24, 1985, 202–214.

Nagy, E., Carey, J.H. and Hart, J.H. 1986. Hydrocarbons in St. Clair River sediments. Water Pollut. Res. J. Can. 1(3): 390–397.

Nagy, E, Carey, J.H., Hart, J.H., Ongley, E. and Tisdale, J. 1986. Hydrocarbons in MacKenzie River suspended sediments. NWRI Contribution 86-65.

Assessment of Significance of Sediment Contaminants — with Emphasis on Areas of Concern in the Great Lakes Basin and the Role of Benthic Invertebrates

T. Reynoldson, Study Leader

T. Reynoldson

INTRODUCTION

In the Great Lakes Basin, 39 of 42 IJC Areas of Concern have documented sediment contamination. However, the quantification of the extent of the contamination is generally inadequate and often based upon one or two chemical analyses of sediment. Sediments have historically been considered a sink for contaminants. They, and the associated biota, frequently have concentrations that are orders of magnitude higher than the water column. Recent research has suggested that sediments may be an important secondary source through biotic and abiotic processes directly to the biota and hence through the food chain or to the water column. The role of benthic invertebrates through a number of processes may be important in mediating contaminant movement. In order to understand the significance of sediment contaminants more fully both the partitioning (i.e., what is where) and cycling (i.e., how fast and where it moves) will be investigated. Emphasis will be placed on both the role of benthic invertebrates and also on anoxia, which frequently occurs at the mud/water interface and can have a profound effect on both chemical and biological processes.

While the potential importance of these processes is accepted,little information is available on the movement of contaminants in Areas of Concern, particularly the role of the biological processes, from sediment to other components of the ecosystem. As a result, the assessment of the significance of contaminants in sediments has not been undertaken to allow proper management decisions on remediation, if necessary, to be made.

This work will establish the importantance of *in situ* sediment contaminants in Areas of Concern; assess methods for testing significance of sediment contamination and recommend an appropriate protocol and associated criteria; and quantitatively determine the significance of various biotic processes in contaminant cycling and partitioning between water, sediment and biota.

RESEARCH RESULTS

Study leader began the project in January; therefore, time was spent establishing and equipping the laboratory, selecting techniques, and determining field and laboratory methodologies:

1. Established rearing and culturing techniques for two organisms, *Hexagenia limbata* and *Chironomus tentans*; developed bioassay capacity for sediments using these organisms.

2. Initiated program to identify non-directional variability in benthic community structure; conducted initial sampling; and developed strategy for long-term sites in eastern, central and western Lake Erie.

3. Identified both temporal and spatial variability in partitioning of contaminants in sediment and benthos of eastern, central and western Lake Erie.

4. Developed techniques using both chemistry and isotope labels to examine uptake kinetics of contaminants from sediment, bacteria, invertebrates and fish.

PUBLICATIONS

Reynoldson, T., Hampel, L. and Martin, J. 1986. Biomonitoring network operated by school children. Environ. Pollut. (Series A) 41: 363–380.

Gannon, J.E., Edwards, C.J., Reynoldson, T.B. and Hartig, J.H. 1986. Indicator approaches used in the Great Lakes International Surveillance Program. IEEE Oceans '86 Conference Proc., Washington, D.C., September 23–25.

Diffusive and Internal Sediment Loadings In Lake Erie

F. Rosa, Study Leader

F. Rosa

INTRODUCTION

It is necessary to understand how and in what quantities sediments and associated contaminants are translocated from the nearshore regions of lakes and bays to the offshore receiving waters. Sediments laden with toxic substances are especially prevalent in the nearshore regions and effective management of such pollutants will require accurate measurements of the fluxes of these materials to the offshore regions. Also vertical flux measurements within the offshore regions are necessary to understand how these contaminants are recycled within the water column, and, if possible, what percentage will eventually achieve permanent burial.

RESEARCH RESULTS

Five sediment traps and six current meter moorings were deployed in the Sandusky basin area to measure the diffusive sediment loading from the bay to the offshore region of the central basin. These traps have been refurbished monthly from May to mid-October. The trapped material has been analyzed for different chemical components. Results show that flux rates decrease with increasing distance from the bay to the offshore area. Also the rates are variable with time of season, with highest rates observed during the fall. Flux rates at the shallowest station closest to the bay showed the highest variability with season. Flux rates of total trapped matter varied from 50 to 300 g/m²/d.

One sediment trap and one current meter mooring were deployed at each of the three basins of Lake Erie, west (W 357), east (E 23), and central (C 84), to measure internal sediment loading during the same time period as above. The flux rates in all three basins show a high seasonal variability for all parameters measured, with the highest rate observed in the fall. The seasonal flux rates for total (TTM), inorganic (ITM), and organic (OTM), trapped matter from April to mid-October are shown in Figure 39. The

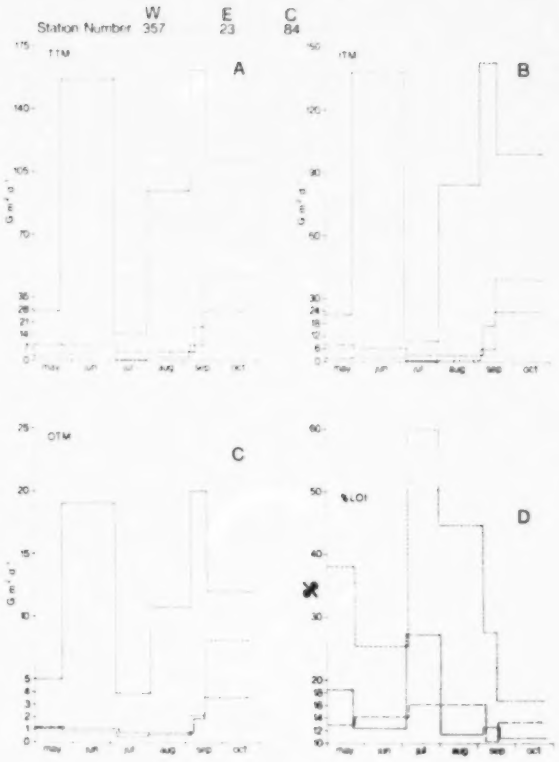


Figure 39. Sedimentation rates of total, inorganic and organic trapped matter, and loss on ignition analysis at 2 m above the lake bottom, in the three basins of Lake Erie (1986).

mean flux rates during the study period were 14, 20 and 95 g/m²/d for the east, central and west basin, respectively. The trapped matter in the central basin always showed a higher percent organic content than the other two basins (Fig. 39-D). The west basin, the shallowest of the three basins, showed the highest flux rates and seasonal variability in all parameters measured, especially for TTM, ITM and OTM (Fig. 39-A, 39-B, 39-C). The difference in the TTM flux rates between the central and east basins was main-

ly due to the inorganic fraction. The higher inorganic content in the east basin was contributed by the eroded central basin bluff material translocated to the east basin by the predominant west to east surface water flow. The lowest flux rates in all three basins were observed during the month of July, when the lake is least affected by wind-induced resuspension of bottom sediments. These results indicate considerable sediment resuspension in the west basin, and mostly inorganic sediment translocation from the central to the east basin.

PUBLICATIONS

Rosa, F. and Burns, N.M. 1987. Lake Erie central basin oxygen depletion rates from 1929 to 1980. J. Great Lakes Res. In press.

Rosa, F. 1987. Lake Erie central basin phosphorus trend analysis from 1968 to 1982. J. Great Lakes Res. In press.

Shertzer, W.M., Saylor, J.H., Boyce, F.M., Robertson, D.G. and Rosa, F. 1987. Seasonal thermal cycle of Lake Erie. J. Great Lakes Res. In press.

Erosion Resistance of Undisturbed and Remolded Cohesive Tills

A.J. Zeman, Study Leader

A.J. Zeman

INTRODUCTION

Quantitative measurements of sediment resistance to erosion are required for interpretation of subaerial and subaqueous erosion that occurs along the shores of the lower Great Lakes consisting predominantly of cohesive sediments of the Late Wisconsin age. The purpose of the research is to express the erosion resistance of several representative sediment types in terms of the critical shear stress and the erosion rate at higher shear stresses. All samples are tested in a rotating-cylinder apparatus developed and calibrated at NWRI. In addition, each sample is tested for basic geotechnical properties that are then correlated with the results of the erodibility tests.

RESEARCH RESULTS

Laboratory erodibility tests were performed on 51 undisturbed samples of cohesive tills from three sites on the north central shore of Lake Erie and from one site on the south shore of Lake Ontario. The samples were taken from toe portions of actively eroding bluffs using a diver-operated till corer. The most consistent results and best correlations with geotechnical tests were obtained using only the critical shear stress to characterize sediment erodibility. The analysis of variance confirmed statistically significant difference for different till formations, while no significant difference was obtained for two different sites three km apart within the same till formation. Although erosion rates measured are highly variable for individual samples, due to the effect of variable surface roughness during the test, averaged values (Fig. 40) show consistent direct relationship between the critical shear stress and the erosion rate. The two Lake Erie tills were found more resistant to erosion, both in terms of the critical shear stress and the erosion rate, than the till from the Stoney Creek site in Lake Ontario. Surface roughness during the erodibility test was estimated from comparisons of test results obtained for five calibration cylinders of known standard surface roughness. The standard surface roughness values for till samples were found to be in the range from 0.0 to 0.5 mm, except for occasional higher values caused by disintegration of samples along existing microfissures.

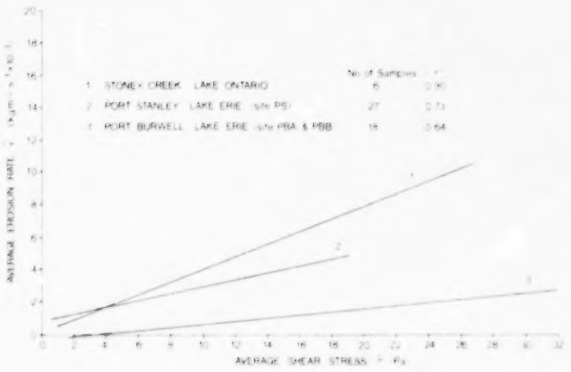


Figure 40. Averaged relationships between shear stress and erosion rate for Lake Erie and Lake Ontario tills.

Most of the erodibility tests described in the literature have been performed on samples that were artificially consolidated prior to tests. A series of tests was therefore undertaken in 1986/87 to determine the effect of sediment remolding and reconsolidation to the same water content as that of undisturbed samples. A consolidation mold was developed for this purpose that permits consolidation of samples to a predetermined water content. The preliminary test results indicate that artificially consolidated samples erode at lower critical shear stress but, on the other hand, their erosion rate values are appreciably lower than those of the undisturbed samples. The interpretation of the test data is currently in progress.

PUBLICATIONS

Zeman, A.J. 1986. Laboratory test of sediment erodibility. Part II - Erodibility tests on undisturbed Lake Erie and Lake Ontario samples. NWRI Contribution 86-113.

Zeman, A.J. 1986. Erodibility of Lake Erie undisturbed cohesive tills. Proc. Symp. on Cohesive Shores, NRCC ACROSES, 150–169.

Coakley, J.P., Rukavina, N.A. and Zeman, A.J. 1986. Wave-induced shear stress and subaqueous erosion of cohesive tills. Proc. Symp. on Cohesive Shores, NRCC ACROSES, 120–136.

Rukavina, N.A. and Zeman, A.J. 1987. Erosion and sedimentation along a cohesive shoreline. J. Great Lakes Res. 13(2): 202-217.

Great Lakes Sediment Data Base

N.A. Rukavina, Study Leader

N.A. Rukavina

INTRODUCTION

More than 4000 surface-sediment samples and cores have been collected by NWRI in the Great Lakes during the period from 1968 to the present. Lakewide data on a grid of 5–10 km are available for all the lakes; nearshore (less than 20-m depth) data are available on a grid of 1-2 km for the lower lakes. This study is developing a computer data base using an expanded NAQUADAT structure for storage and retrieval of the data which currently exist in a variety of electronic and non-electronic formats. The primary application of the data base will be as an archive of valuable historical sediment data required for various internal and external research, engineering and environment assessment studies.

RESEARCH RESULTS

Progress to date consists of the definition of the file structure, the acquisition of the data to be entered, and the completion of a contract to edit the data, create the file and develop retrieval and updating procedures. A usable data base now exists as part of the NAQUADAT file which contains sedimentologic and geochemical data from the regional geology surveys of Lakes Ontario, Erie, Huron and Superior and the nearshore surveys of Lakes Ontario, Erie and Huron. Table 4 shows the file structure and contents.

Table 4. Great Lakes Sediment Data Base — General Report Structure

BLOCK 1- SERIAL NUMBER

BLOCK 2- FIELD DATA

BLOCK 2A
LAKE FIELD STA. NO. LATITUDE LONGITUDE DATE TIME OF DAY TIME ZONE WATER DEPTH

BLOCK 2B
FIX SYSTEM ACCURACY SOUNDER SAMPLER SAMPLE THICKNESS ARCHIVE SAMPLE SAMPLE PHOTO

BLOCK 3-STRATIGRAPHY
UNIT NO. TOP-BOT CM COLOUR CONSISTENCY STRUCTURE COLOUR TEXTURE PEBBLE TYPE SUBSTRATE
1
2
ETC.

BLOCK 4
SUBSAMPLE ANALYSED TOP BOTTOM %

BLOCK 5- GRAIN-SIZE DATA
GRAVEL SAND SILT CLAY MEAN SIZE SORTING SKEWNESS KURTOSIS

BLOCK 6- CHEMICAL DATA

BLOCK 6A- GENERAL
TEMPERATURE PH EH CLAY MINERALS

BLOCK 6B- XRF DATA %DRY WT
SIO2 AL2O3 FE2O3 MGO CAO NA2O K2O P2O5 MNO S

BLOCK 6C- LECO DATA %DRY WT
TOTAL C ORG C

BLOCK 6D- AAS DATA PPM UNLESS OTHERWISE NOTED
HG PPB PB CU ZN NI CD

FE V SR AS MO SE

ZOE TOE DOT P/B PPB DIE. ENDO

NAP ASP ORG P TOT P TOT N C/N RATIO

BLOCK 7- NARRATIVE

PUBLICATIONS

Fellowes, M. 1987. Establishing a sedimentology data system on the Cyber 280 computer. Report for Contract Study KW405-6-1785 on behalf of the NWRI Hydraulics Division.

Rukavina, N.A. and Mudroch, A. 1987. Definition of NAQUADAT codes for the Great Lakes sediment data base. NWRI Hydraulics Division Technical Note 87-1.

Contaminant/Nutrient Relations in Settling Material

M.N. Charlton, Study Leader

B.G. Oliver

M.N. Charlton

INTRODUCTION

One of the important interactions between the nutrient and contamination issues in the Great Lakes is the possible control of contaminant sedimentation by nutrient-related algal growth. Most contaminants are stored in bottom sediments to some degree. While chemicals absorb onto clays and other soil particles, they also are absorbed by algae and bacteria. Some of these cells die and fall into the bottom sediment where they contribute to the organic fraction. In the study of nutrient loading effects, it has been noticed that the proportion of loaded phosphorus retained in the lake is related to the depth and flushing. This means that P loading promotes sedimentation through the proliferation of algae cells. The purpose of this study was to investigate the possible links between the seasonal algal cycle and contaminant sedimentation.

RESEARCH RESULTS

The rate of downflux into sediment traps in Lake Ontario appears independent of productivity cycles as the winter rates are at least twice the summer rates at all depths. This is inconsistent with the hypothesis that the lake productivity, which is higher in the summer, is the main factor driving vertical fluxes. Sediment loading and resuspension seem to be critical components which complicate discovery of the importance of algal death and settling. The concentrations of many organic compounds were measured in winter and summer sediment trap samples from 1980 to 1986. Generally, winter concentrations of organics were higher than in the summer. Compounds such as αBHC (isomer of Lindane) seem to partition into organic matter in the summer (Fig. 41). Between the winter of 1983 and the summer of 1986, there seemed to be some indication of a downward trend in the total PCB concentration in the sediment traps (Fig. 42), but more data are needed to be certain of this. Sediment traps were installed in Lake Huron, Lake Superior, Lake St. Clair, Lake Ontario and the outlet of Lake Ontario. Table 5 shows that

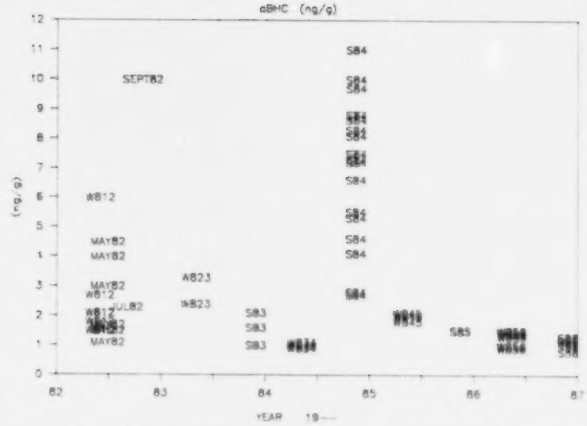


Figure 41. Winter (W) and summer (S) concentrations of α BHC (ng/g) in sediment traps in Lake Ontario (W823 = winter 1982/83).

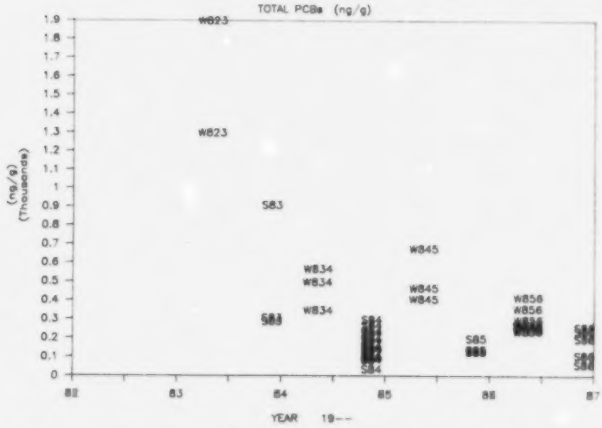


Figure 42. Winter (W) and summer (S) concentrations of total PCBs (ng/g) in Lake Ontario sediment traps.

using the traps even for a short period provides a way to collect ambient seston for chemical analyses. For example, the traps in Lake Superior were in place for only one week. These samples are being analyzed for organic contaminants. Results have shown that the trap contents are similar to surficial sediments and probably provide the

earliest indicator of contaminant sedimentation. For monitoring purposes, the best exposure period seems to be summertime, when the effects of the resuspended components are minimized.

Table 5. Sediment Trap Catch Rates - 1986

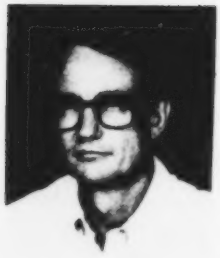
Lake	Exposure Days	Catch Rate $g/m^2/d$
SUPERIOR	6	0.7
HURON	100	1.0
ONTARIO	177	0.2-1.0
ST. CLAIR	14	8-688

PUBLICATIONS

Oliver, B.G., Charlton, M.N. and Durham, R.W. 1987. Distribution, redistribution and geochronology of PCB congeners and other chlorinated hydrocarbons in Lake Ontario sediments. NWRI Contribution 87-25.

Rivers Research Branch

E.D. Ongley, Director



E.D. Ongley

The Rivers Research Branch (RRB) provides an institutional focus for research, applications and policy advice for a broad range of water resource activities that are associated with rivers and river basins in Canada.

RATIONALE

Water resource management in Canada is carried out within the framework of land-water interactions. This interaction is manifested in rivers which receive and integrate a multitude of anthropogenic activities. These activies are associated with point sources such as effluents from urban and industrial waste-disposal facilities, storm drains and other direct inputs into the riverine environment, and from a wide range of nonpoint sources such as atmospheric deposition, groundwater contamination, agricultural chemicals, urban runoff, etc. Rivers are the primary means by which these impacts are transferred to large lakes and oceans.

Rivers are also the focus of a variety of man-made and natural physical phenomena which can have major economic implications. These include engineering activities such as dams, diversions and channel modifications; ice jams, which cause severe flooding, and ice particles (frazil ice), which can severely reduce the hydro-electric potential of northern rivers.

The RRB seeks to understand complex relationships involving physical, biological and chemical interactions in Canadian rivers. This knowledge base is required to meet federal obligations for current and emerging water resource management concerns having national and international implications.

BRANCH STRUCTURE AND FOCUS

The RRB is structured around six research projects. These encompass the Long Range Transport of Airborne Pollutants (LRTAP), Water Quality Monitoring/Modelling, Contaminants/Pesticides, Groundwater Contamination, Water Quantity Modelling/Monitoring and Ecotoxicology. Projects facilitate multidisciplinary research yet preserve the critical mass of disciplinary expertise.

The LRTAP Project is responsible for research into hydrological and chemical interactions from acid rain; tracking American aquatic-effects modelling activities and developing Canadian alternatives to U.S. positions; and evaluating large-scale patterns of risk to Canadian freshwater resources from acid rain under alternative emission scenarios. This project provides national leadership in the science of LRTAP monitoring and assessment and provides expert opinion on international research activities which may have an impact on Canadian negotiating positions.

The Water Quality Monitoring/Modelling Project provides a framework for mathematical and physical research leading to improved data analysis protocols, predictive modelling of physical and biogeochemical processes and more cost-effective monitoring of the nation's rivers. This project provides mathematical and modelling support to the LRTAP project, expertise in taste and odor problems of drinking water and develops innovative remote sensing techniques to monitor water quality.

The Contaminants/Pesticides Project provides a focus for research into characteristics of toxic organic and inorganic chemicals in Canadian rivers and the evaluation of chemical pathways, fate and effects at the organism, community and ecosystem level. This project provides leadership in hazard assessment for pesticides and selected toxic substances, and delivers the NWRI commitment to Environment Canada under the Environmental Protection Act and the Pest Control Products Act.

The Groundwater Contamination Project provides national leadership in the fields of hydrogeology, contaminant migration, aquifer decontamination, waste site restoration and site decomissioning technology.

The Water Quantity Modelling/Monitoring Project carries out research on the physical parameters of rivers that may be altered by anthropogenic activities or natural processes. This project provides the hydraulic and modelling expertise to study problems such as contaminant transport by sediments and nonpoint sources of pollution. River engineering applications and advisory services have widespread application, particularly those arising from water resource interventions that have significant economic implications.

The Ecotoxicology Project seeks to provide ecological meaning to aquatic chemical data. This project develops practical and cost-effective methods for determining toxic stress in ambient aquatic environments including new methods for inferring mutagenic, teratogenic and genotoxic potential. This project will provide leadership in developing a new generation of water quality guidelines and objectives based on measures of biological response rather than on conventional single-chemical criteria.

BRANCH STRATEGIC GOALS

Collectively, the projects have three strategic goals.

1. Carry out and publish original research and information synthesis on priority issues.

2. Transfer knowledge, advice and technology to lead agencies and to the private sector, as appropriate.

3. Provide expert advice to the Canadian water management community, contribute to national water policies, and represent federal interests in bilateral and international negotiations.

The first goal is the basis for delivering the second and third goals.

Long Range Transport of Airborne Pollutants

D.S. Jeffries, Project Chief

D.S. Jeffries

The ultimate goal of the NWRI Long Range Transport of Airborne Pollutants (LRTAP) Project is to provide a central support for Environment Canada's development and implementation of policy with regard to control of acid rain through emissions reduction, specific ecosystem protection, etc. The project seeks to meet this goal by providing sound, and, as far as possible, up-to-date scientific information and advice on which policy alternatives can be assessed and appropriate decisions made. Specifically, work is directed towards:

1. prediction of the consequences of various emission reduction scenarios with respect to surface water acidification (or recovery from acidification);

2. identification and investigation of critical knowledge gaps, and

3. keeping abreast of new or developing scientific concepts relating to the LRTAP issue.

The broad goal of providing scientific support for departmental policy formulation translates into the following scientific objectives.

1. Develop and refine ecosystem simulation models that can be used to assess aquatic impacts in both space and time, and use them to evaluate remedial strategies and policy options, to synthesize information, and to act as a control of data quality.

2. Develop a quantitative understanding of the hydrogeochemical factors that control the process of acidification in specific watersheds. Comprehension of the acidification process is necessary to develop and validate the models above and assess effects on the biological system, both aquatic and terrestrial.

3. Define the proportion of the Canadian aquatic resource at risk from LRTAP on both a spatial and temporal basis through long-term acidification monitoring. Present and future monitoring will provide the only direct evidence of the influence of emission reductions on aquatic systems.

Geochemical Controls of Aquatic Response to Acid Rain

D.S. Jeffries, Study Leader

R.G. Semkin and M.C. English (University of Waterloo)

INTRODUCTION

Many geochemical factors control the rate at which the sensitive terrain typical of most of eastern Canada responds to acid rain. In particular, the regional manifestation of these factors is poorly understood and even less well documented. Also, the ecologically important short-term acidification that accompanies spring snowmelt is poorly understood. The purpose of this study is to investigate those geochemical, meteorological and hydrological factors that influence ecosystem response to an acid rain stress.

RESEARCH RESULTS

A high quality data base containing contemporary water quality information for over 7000 lakes in eastern Canada was used to evaluate chemical evidence for acidification occurring in response to acidic deposition. Distribution statistics for important water quality parameters in eight subregions of eastern Canada show that the Maritime provinces contain the highest proportion of acidic lakes even though the highest deposition occurs in southern Ontario and Quebec. A more readily available geochemical supply of acid neutralizing capacity at the latter locations explains this observation. However, consideration of the ion ratio (alkalinity: calcium + magnesium, see Fig. 1) shows that the geographical pattern of acidification is a function of both deposition and terrain sensitivity. The ratio shows that a large area of south-central Ontario and southern Quebec has been acidified. The most dramatic evidence of acidification occurs in southern Nova Scotia and New Brunswick. Northwestern Ontario and Labrador show little evidence of the acidification effect.

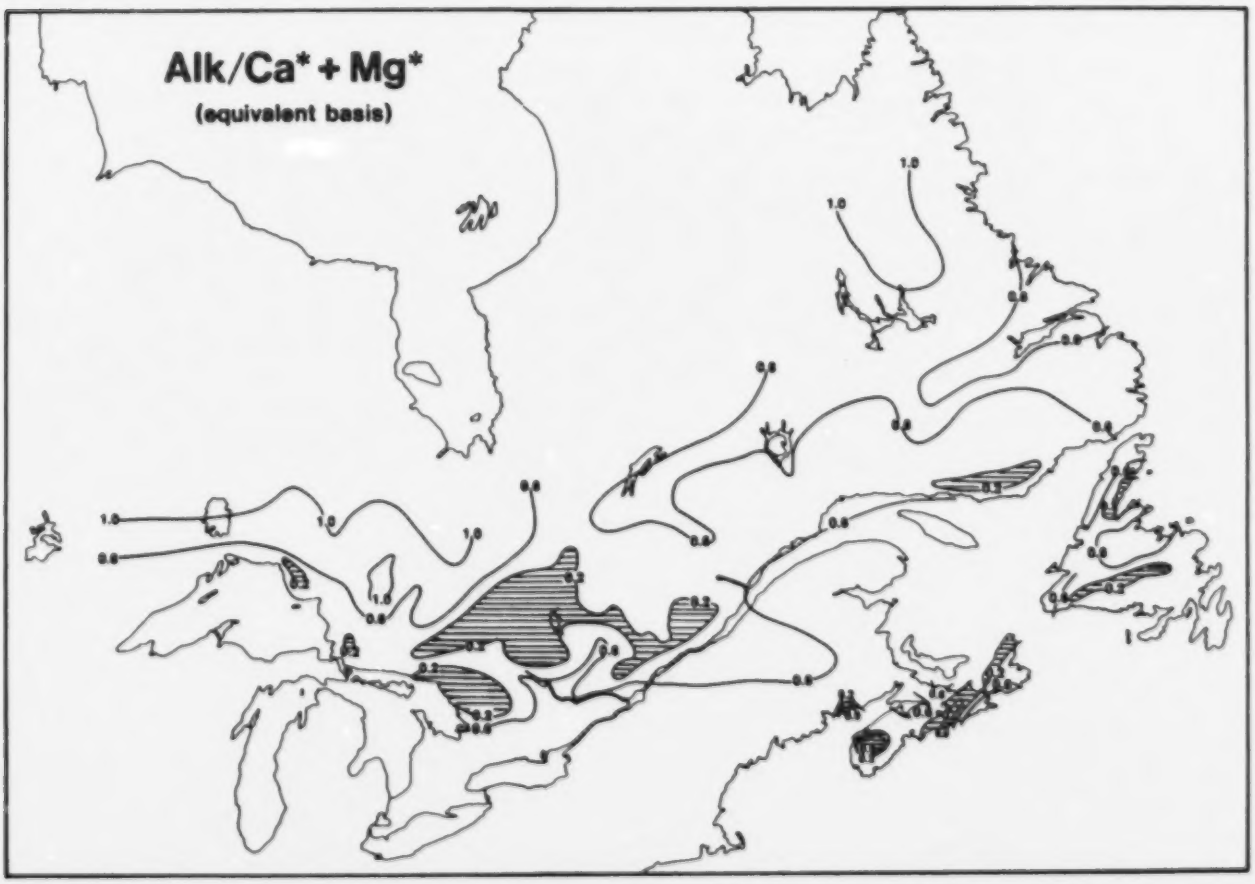


Figure 1. Geographical distribution of the Alk: Ca + Mg ratio across eastern Canada. Cross-haiched areas exhibit the most pronounced indication of surface water acidification.

Comprehensive measurement of the mass balance of a small (1 m^2) snow lysimeter has shown that the meltwater quality leaving the base of the snowpack is strongly influenced by the occurrence of rain. During the melt period, water and chemical input from rain passes directly through the snowpack with little interaction. Spring melt periods with little rainfall occur infrequently at this location; however, when they do, differential elution of ions from the pack is observed, i.e., 50%-60% of H^+, SO_4 and NO_3 are removed with the first 20% of the water. The stream concentration of ions varies greatly throughout the spring melt period with the notable exception of SO_4. Minimum pH correlates with maximum flow rather than periods of differential elution.

Four multilevel piezometer nests were installed at the base of the hillslope adjacent to the shore of Little Turkey Lake. ^{222}Rn determined in groundwater samples extracted from these piezometers during the 1986 melt varied greatly, both between nests and between differing depths within a nest. As expected, deeper groundwaters generally had higher ^{222}Rn concentrations. One mechanism hypothesized for the generation of high stream flows during spring melt is "piston flow" or "groundwater ridging" in which increased capillary pressure causes an increased contribution of deeper groundwater to surface runoff. If this mechanism is in operation, then the high ^{222}Rn initially present in deep piezometer should subsequently appear in the shallower wells. Our data provide little evidence supporting the occurrence of piston flow at the Little Turkey Lake slope site. For example, Figure 2 presents the temporal variation in ^{222}Rn in deep [4 and intermediate (2.6 m)] depth piezometers from nest "B"; the snowmelt hydrograph from lysimeter subplot 1 is also displayed. The only evidence of piston flow apears during the earliest part of the snowmelt season. When meltwater production was at a maximum, ^{222}Rn was at a minimum in both the intermediate and deep piezometers; therefore, dilute snowmelt waters percolate to depths exceeding 4 m in the TLW. Furthermore, the ^{222}Rn pattern is similar for both piezometers when the data for the deeper well is offset backwards by four days (as it is in Fig. 2) implying that it takes four days for the influence of meltwater percolation to be transmitted from 2.6 m to 4.3 m depth in the glacial till. Finally, correspondence of NO_3 concentrations in soil lysimeters, shallow piezometers and littoral zone waters of Little Turkey Lake suggests that most of the water draining from the slope during spring melt flows through the upper 1 m of the soil-till matrix.

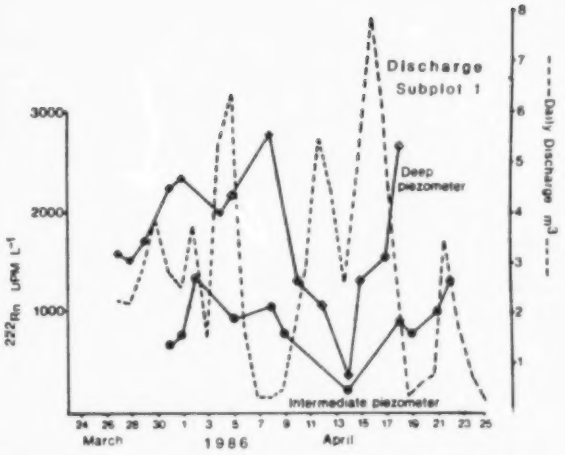


Figure 2. Radon concentrations in piezometer nest B and meltwater discharge from subplot 1.

PUBLICATIONS

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Hydrogeochemical Response of the Turkey Lakes Watershed to LRTAP

R.G. Semkin, Study Leader

D.S. Jeffries, R. Neureuther, M. Seymour and J. Gough

R.G. Semkin

INTRODUCTION

The long-range transport of airborne pollutants is recognized as a major environmental threat to the sensitive ecosystem that covers most of eastern Canada. In order to understand the biogeochemical processes occurring during acidification of lake basins, a whole-ecosystem study was established in which these processes can be monitored in detail. To this end, ion mass budgets were determined for the chain of lakes contained within the Turkey Lakes Watershed (TLW) and analyzed to determine the relative importance of the various acidifying species, their dominant input pathways and the biogeochemical mechanisms by which the catchment ameliorates their effects. The TLW is an undeveloped, forested (deciduous) catchment located on the Canadian Shield, 50 km north of Sault Ste Marie, Ontario. Annual SO_4 deposition is usually > 30 kg $SO_4.ha^{-1}$.

RESEARCH RESULTS

Lake budgets have been calculated for two water years, i.e., June 1981–May 1983. Input components included direct atmospheric deposition, measured stream loadings and an estimated terrestrial basin loading for the ungauged portion of the watershed. Output for each lake was measured at the outflow gauging station. Total precipitation quantity was similar for both water years (1304 and 1369 mm respectively); however, the pattern was very different. The 1981/82 water year began with extremely heavy rainfall in June, followed by a dry summer and autumn, and finished with a late spring melt episode. The stream hydrographs for this period were characterized by a few short-term, high-intensity flow events and rather extended periods of low "base flow" during summer, autumn and winter. In contrast, the 1982/83 water year experienced a very wet autumn, a warm winter and multiple spring melt episodes. Hydrographs in 1982/83 consequently contained several peaks of moderate flow intensity and higher base flow than observed the previous year. If the base flow intensity is indicative of the groundwater flux present in the basin, then the lakes probably received greater groundwater input during 1982/83 compared to 1981/82.

Table 1 presents ratios of total output to total input for water and selected ions for each of the lakes. Water budgets for Turkey Lake and Batchawana Lake South (1981/82 only) are in balance. Wishart Lake consistently exhibits a small deficit of output over input, while Little Turkey Lake is opposite with a larger excess of output over input. In order to explain the observed imbalances in water budgets for Wishart and Little Turkey lakes, there must exist a small unmeasured output component for the former and a larger unmeasured input component for the latter. We believe that groundwater seepage can account for both situations; the degree of imbalance was larger in the second water year when the groundwater component of stream runoff was also larger, as noted above.

The chemical budgets show that deposition directly to the lakes' surfaces is the major input pathway for H^+ and NH_4. Both atmospheric deposition and export from the terrestrial watershed are important sources for NO_3, while the terrestrial watershed is the major source for Ca, ANC, and SO_4. In the TLW, the terrestrial basin strongly retains NH_4, but not NO_3; that is, the nutritional requirement of the forest seems to be primarily satisfied by the former. The strong retention of NH_4 and mobility of NO_3 means that both species (along with H^+, of course) are acidifying agents in the TLW.

Table 1. Ratio of total measured output to total measured plus estimated input for Batchawana Lake South, Wishart Lake, Little Turkey Lake, and Turkey Lake for the 1981/82 and 1982/83 water years.

		Water	H^+	Ca	NH_4	ANC	SO_4	NO_3
Batchawana	81/82	1.0	0.1	1.2	0.6	2.3	1.0	0.7
Lake South	82/83	1.1	0.2	1.5	0.9	4.7	1.1	0.9
Wishart	81/82	0.9	0.1	0.9	0.7	1.1	0.9	0.7
Lake	82/83	0.9	0.1	0.9	0.6	1.2	0.9	0.8
Little	81/82	1.2	0.1	1.3	0.3	1.7	1.2	0.9
Turkey Lake	82/83	1.2	0.1	1.4	0.2	1.7	1.2	0.9
Turkey	81/82	1.0	0.0	1.1	0.8	1.5	1.0	0.7
Lake	82/83	1.1	0.0	1.3	0.6	1.6	1.1	0.7

By comparing the ratio for chemical species in Table 1 with that for the corresponding water budget (i.e., "normalizing" for water budget imbalances), it is clear that the lakes themselves all strongly retain H^+ but only partially (and variably) retain the nitrogen species. Sulfate outputs balance inputs across all lakes, as do other ions not included in these tables. In contrast, there is a net excess of Ca and ANC output over input in almost all cases. Once again we believe that the greater influence of groundwater inputs in the second water year is manifested by the greater budgetary imbalances observed during that year. In particular, the budgets for Little Turkey Lake require a large unmeasured input of both Ca and ANC, and strong concentration gradients at the sediment-water interface, both for these ions and Cl (a good groundwater tracer), provided further evidence of inbound groundwater seepage. It should be noted, however, that Ca exchange at the sediment-water interface is known to occur in the TLW and it is functionally difficult to distinguish this mechanism from a groundwater input.

There is generally a greater budgetary excess of ANC than Ca. Sometimes the excess is balanced by other base cations not included in Table 1. In other instances, another ANC-generating mechanism is needed. Irreversible SO_4 reduction also provides ANC; however, our budgets suggest that SO_4 is in balance. Perhaps this is fortuitous, since groundwater seepage would also carry SO_4 with it, thereby supplying the necessary "raw material" for ANC generation by the SO_4 reduction mechanism. In any event, SO_4 reduction is unlikely to be a major contributor to the ANC supply for these lakes since they have very short water renewal times (0.15 - 1.3 yr).

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Sulfur: Its Forms and Isotopic Composition in Acid Sensitive Lakes

J.O. Nriagu, Study Leader

R.D. Coker, D. Holdway and H.K.T. Wong

J.O. Nriagu

INTRODUCTION

Although naturally produced organosulfur compounds contribute to the acidity of rainfall, we know little about their distribution in, or release from, Canadian lakes and wetlands. This study was aimed at providing the first set of measurements on the concentrations of volatile organosulfur compounds in selected bogs and lakes of Ontario.

Variations in stable sulfur isotopes can be used to fingerprint the sources, dispersion pathways and ultimate sinks of pollutant sulfur in lakes. The isotopic technique was applied to the study of sulfur cycling in the watersheds at Algoma (Turkey Lakes) during this fiscal year.

RESEARCH RESULTS

A sensitive and robust technique was developed for determining the low levels of volatile organosulfur compounds, specifically dimethyl sulfide (DMS), in lake water samples. The detection limit for the technique was better than 0.6 ng/L DMS in lake water. Using this method, the average DMS concentration in 14 representative bogs of Ontario was found to be about 360 ng/L. The release of DMS from the bogs was estimated to be quite high—about 310 mg/(m^2·yr)—implying that such ecosystems represent an important source of the acidifying sulfur compounds in the air at remote areas of the country.

By combining the results of DMS measurements with the long-term isotopic data of bulk precipitation samples, we have estimated that biogenic sources can account for up to 30% of the acidifying sulfur burden in the atmosphere in remote areas. The data also point a significant biological re-emission of anthropogenic sulfur; the role of this process in continuing the acidification of the environment even after reductions in industrial SO_x emission rates is believed to be a matter of some concern.

PUBLICATIONS

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Aquatic Effects of Acid Precipitation: Models and Monitoring

M.E. Thompson, Study Leader

M.E. Thompson

INTRODUCTION

Under the terms of the Canada/U.S. Memorandum of Intent (MOI) concerning transboundary air pollution, the effects of acid deposition must be quantified and rigorously defined. Modelling activities of rate-related effects are vital components of this activity.

The cation denudation rate (CDR) model was used in the above-mentioned MOI to predict pH changes to be expected if acid deposition decreased, and therefore validation of the CDR model is an ongoing activity.

RESEARCH RESULTS

Comparison of the excess sulfate yields of rivers in Atlantic Canada, 1971–73 and 1982–84, shows a decrease of about 50% in the latter years, in accord with records of emissions in Canada and the U.S.A.

The CDR model continues to work well, whether it is applied to data for rivers in Atlantic Canada or in Ontario.

PUBLICATIONS

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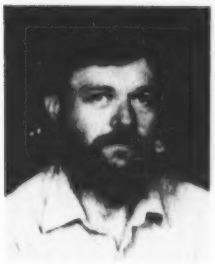
Origin of Organic Waters and their Impact on Aquatic Ecosystems

R.A. Bourbonniere, Study Leader

R. Peterson (Fisheries and Oceans, St. Andrews)
T. Pollock (Water Quality Branch, Moncton) and
I. Kessel-Taylor (Inland Waters/Lands Directorate, Ottawa)



R.A. Bourbonniere

INTRODUCTION

This study relates directly to the critical problem of apportioning the acidity of lakes and rivers to natural and anthropogenic sources. Dissolved organic materials (DOM) contribute to the natural acidity of colored waters in eastern Canada. DOM has also been shown to be effective in complexation of metals (especially Al). This study seeks to quantify natural organic acidity and investigate the relationship between the chemistry of aluminum-DOM complexes and their biological activity. In this way we may be able to understand how DOM protects fish from the toxic effects of Al.

Another aspect of the study relates to the interaction between aquatic ecosystems and their watersheds with respect to the acidity and metal complexation questions. This includes the impact of wetlands on aquatic ecosystems downstream, and relates as well to the development of peatlands for fuel or other uses. Our understanding of the processes controlling DOM in aquatic ecosystems can be useful in building watershed acidification models.

RESEARCH RESULTS

The major findings to date relate to the character of DOM fractions isolated from 160 natural water samples collected at three study areas in eastern Canada (Barrington Bog, N.S., Kejimkujik National Park, N.S. and Sept-Îles, P.Q.) between July 1984 and March 1986.

1. On average, about 60% of the dissolved organic carbon (DOC) in the waters sampled resides in the acidic fractions of DOM.

2. Among the three acidic fractions, hydrophobic acid (HPOA) is dominant, humic acid (HA) ranks next in abundance, and hydrophilic acid (HPIA) is least.

3. Variations in the relative distribution of the acidic organic fractions occur with sample type (bog, lake, river, etc.) and season, and, to a lesser extent, with hydrologic condition.

4. Titration acidity determinations on these isolated organic fractions indicate that the HPIA fraction contains a much greater number of acidic fractions per unit of organic carbon than the other two, and may provide significant organic buffering to some colored waters.

PUBLICATIONS

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Operational Acid Precipitation Models: Review, Enhancement and Application to LRTAP Monitoring

A.S. Fraser, Study Leader

A.S. Fraser

INTRODUCTION

This study has been the objective of determining the linkages between aquatic effects and terrestrial sensitivity under the Long Range Transport of Airborne Pollutants program for regions of Canada such as Quebec, the Maritimes and the West, applying risk assessment analysis techniques to regions of Canada. As an adjunct the LRTAP monitoring program will be evaluated in light of recent research results and evolving requirements.

RESEARCH RESULTS

The assessment of aquatic resources at risk for the province of Quebec has concentrated on the linkages between terrestrial and aquatic regimes. Terrestrial data indicates that the vast majority of terrain on the northern side of the St. Lawrence River in Quebec is sensitive to acidic deposition, whereas the Eastern Townships are less sensitive. Terrestrial information in the region of study has been assessed and yielded a composite rating based upon a scale of high, medium and low potential to reduce acidity. The study area was assessed at the Water Survey of Canada tertiary drainage level with all necessary and available water quality data from the NAQUADAT system used. Where sufficient ANC (acid neutralization capacity) data were available, an aquatic factor scaled to the same proportions as the terrestrial factor was calculated. An average relative error of 0.34 was computed for the terrestrial/aquatic relationship, indicating that the terrestrial data could accurately predict the aquatic effects due to LRTAP approximately 65% of the time. By further manipulations and optimization techniques, the relative error has been reduced to 0.29. Activities are currently under way to further reduce the error term.

Based upon the results provided by the microcomputer system RAISON, which was used to spatially evaluate the data by watershed, for distributions of ANC, an aquatic risk assessment for Quebec estimates that south of latitude 52° N, 5% of the lakes exhibit effects of strong acidification, with an additional 34% considered under stress from LRTAP-related activities.

Activities under this project will provide a quantitative linkage between the aquatic and terrestrial components, thereby allowing estimates of aquatic risk to be estimated in regions for which only limited aquatic data are available due to accessibility for sampling. Future activity will also include the estimation of risk assessments for other regions of Canada such as the Maritimes and the West coast. Model applications for control strategies will be evaluated and recommendations for aquatic risk reduction will be made.

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Dissolved Metal Species in Acid Sensitive Lakes of Nova Scotia

H.K.T. Wong, Study Leader

J.O. Nriagu, R.D. Coker and J.J. Kerekes (Canadian Wildlife Service)

H.K.T. Wong

INTRODUCTION

The processes of pollutant metal transfer from the atmosphere to the lake water and to the sediment column is basic to our understanding of the impact of acid rain on the trace metal cycle. The study during this fiscal year focuses on the partitioning of metals (especially Al) between the dissolved and solid phases close to the sediment-water interface. Also, many pollutant metals are closely associated with organic matter in a lake ecosystem. A study of Al, Pb and other toxic metals in organic fractions in the water and sediments under different natural pH conditions should reveal the influence of metal-organic interactions on the release of acidification.

RESEARCH RESULTS

An automated method for the analysis of dissolved aluminum species in lake waters and sediment porewaters was developed. Interlaboratory calibrations were also carried out and the results were satisfactory.

In situ porewater samples were recovered from sediments at selected basins of Kejimkujik (organic rich water) and Mountain (clear water) lakes in Nova Scotia. The pH, alkalinity, DOC, Total-Pb, Total-Al, Total Reactive Monomeric-Al, Organic Reactive Monomeric-Al and Inorganic Reactive Monomeric-Al were measured. Preliminary results show that only 10% to 30% of the total dissolved Al in the porewaters of Kejimkujik Lake is reactive and that most (70% - 90%) of the reactive Al is bound to the organic matter. The total dissolved Al concentration increases with depth below the sediment-water interface; on the basis of a simple diffusion model, the release of soluble Al from the sediments is estimated to be 375 mg / m^2/yr for Kejimkujik and 102 mg / m^2/yr for Mountain Lake. These fluxes point to sediments as an important source of "dissolved" Al in the lake water. The results also suggest that a significant amount of Zn (about 4 mg / m^2/yr) are released from the Kejimkujik Lake sediments. It will be interesting to compare the external input of Zn and other trace metals with the rate of regeneration from the sediments.

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Water Quality Monitoring/Modelling

D.C.L. Lam, Project Chief

D.C.L. Lam

ISSUES

The water quality in many river systems in Canada has been adversely affected not only by chemical effluents from point source discharges, but also by nonpoint source pollutants of agricultural, atmospheric and urban origin. The management strategies for better water quality in these river systems requires an integrative approach that can summarize complex disciplinary research results. Of specific concern is the establishment of the accurate assessment of damages to river ecosystems due to these contaminants. Through the use of monitoring data and the integrative approach, the quantification of pollutants from different sources, their pathways and fate, and their ecological impacts are highly pertinent to water quality management in river basins. Thus, based on sound scientific methodologies, recommendations on pollution abatement strategies, monitoring protocols, scenario studies and post-audit analyses of remedial actions are required. The Municipal-Industrial Strategy for Abatement (MISA) program has placed a strong emphasis on modelling and monitoring techniques for an accurate environmental assessment.

RATIONALE

The use of validated water quality models and monitoring protocols in developing and testing management strategies has been instrumental in the phosphorus control program. Recommended control measures for agricultural practices, i.e., no-till, etc., require a modelling capability that can link land use to fine sediment transport and subsequently to phosphorus bioavailability in the aquatic ecosystem. Similarly, the emission of sulfur and nitrogen oxides into the atmosphere and their re-entrance into terrestrial and aquatic regimes via the hydrological cycle require a modelling framework that can link the atmospheric load to the water quality conditions in streams and rivers. The same framework is also required in understanding the pathways and fate of pesticides and other contaminants through the terrestrial and aquatic regimes in river basins. Thus, an economical and effective approach to develop such modelling and monitoring research capabilities is to form a unified research project that combines the computational, statistical and experimental experts in these areas to address the problems.

LONG-TERM OBJECTIVES

To develop knowledge and expertise to enhance understanding, simplification and rationalization of water quality monitoring and management programs in Canadian river basins. This strategic goal has several dimensions.

1. Develop the knowledge and practical capability to rationalize complex land-water interactions through the development of a variety of models, and by statistical, physical and chemical research. This entails two principal activities: (i) use of physical and mathematical models to better understand the interaction of complex variables, and (ii) the use of synthesis modelling to simplify complex interactions for environmental management purposes.

2. Transfer to government and private sector clients, simulation and synthesis techniques and environmental sensing devices and protocols. These enhance the ability of water resource managers to make cost-effective judgments about policy options involving atmospheric/land/water interactions of Canadian river basins.

3. Provide expert advice on river basin pollution issues, especially those for which there are significant federal concerns.

SHORT-TERM OBJECTIVES FOR 1987/88

Consistent with the strategic goal, objectives for 1987/88 are:

1. Continue model development for synthesis of land-water interactions in the field of LRTAP in Ontario, Quebec and Atlantic regions. Develop statistical methods for dealing with complex data sets, and apply optical and electronic theory to develop improved means of measuring important physical and chemical variables in river systems.

2. Transfer information synthesis technology to a variety of clients, including model applications to federal-provincial programs of MISA, water quality data collection and interpretation programs of Western and Northern Region and the Sediment Survey, pollutant loading in the Fraser River, and applications of mathematical modelling to pesticide transport in groundwater.

3. Provide expert advice on a variety of issues of federal concern for which policy guidance is essential. Examples include toxics transport in the north Saskatchewan and Mackenzie rivers, contaminant pathways in selected areas of concern tributary to the Great Lakes, and transboundary pollution issues such as LRTAP.

River Water Quality Modelling

D.C.L. Lam, Study Leader

A.G. Bobba, C.R. Murthy and J. Carey

INTRODUCTION

The water quality conditions in many river systems in Canada have been strongly affected by chemical effluents from municipal, industrial and sewage sources. The recent formation of the MISA (Municipal-Industrial Strategy for Abatement) program requires the use of advanced modelling techniques for an accurate environmental assessment for several pilot sites in Ontario. This study is part of the federal effort and focuses on the development of simulation models with predictive capability for the assessment of water quality in river systems including contaminant transport and fate, sediment processes and chemical kinetics.

RESEARCH RESULTS

The chlorobenzene model for the Niagara River has been tested with data collected in 1983. The model is based on a simple adsorption-desorption equilibrium approach. Results showed that the model was able to explain up to 75% of the variance in the observed chlorobenzene data for both the dissolved and the particulate phase. Model results on mixing rates in the sediment near the Niagara River were also confirmed and observed ^{210}Pb data. This simple approach is also applied to the Fraser River, where the contaminant under study is chlorophenol. A model incorporating both the river discharge and the tidal influence has been applied to the river, in cooperation with the Institute of Ocean Sciences, Sidney, B.C.

PUBLICATIONS

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Watershed Models

A.G. Bobba, Study Leader

D.C.L. Lam and D.S. Jeffries

A.G. Bobba

INTRODUCTION

The emission of sulfur and nitrogen oxides into the atmosphere and their re-entrance to the terrestrial and aquatic regimes via the hydrological cycle requires a watershed modelling approach. Not all acidic deposition enters the rivers and lakes directly; most undergo chemical changes in the soil layers before reaching the streams. To quantify the impact of acidic deposition requires the understanding of these watershed processes. Thus, model results need to be verified extensively with data collected from a number of catchments in Ontario, Quebec and the Atlantic region. The results are used for establishing an accurate environmental assessment of the acid deposition impact in eastern Canada.

RESEARCH RESULTS

A simple, three-soil-layer model has been developed and verified with runoff data from the Turkey Lakes, Lake La Flamme, Harp Lake, Mersey River and Northeast Bond River Watersheds. The model was able to explain up to 85% of the variance in the observed data. A four-variable hydrogeochemical model was then linked to the hydrological model. The linked model was shown to explain up to 75% of the variance in the observed stream chemistry data. In particular, it was found that the soil partial pressure of carbon dioxide influenced the model results the most. Sulfate adsorption was found to be moderate in the watersheds tested. Three different classes of watersheds can be identified from the hydrological model results according to the estimated water residence times in the watershed. These residence times are useful for predicting the acidification of the streams and lakes in the watershed.

PUBLICATIONS

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Sources of Taste and Odor Compounds in Drinking Water Supplies

B. Brownlee, Study Leader

G.A. MacInnis and M.E. Fox

B. Brownlee

INTRODUCTION

Taste and odor problems have occurred at one time or another in the water supplies of several municipalities which, together, serve more than one million Canadians. Since 1983, we have been doing research to help municipal and provincial agencies understand and deal with these problems. Our work has focused on identifying specific organic compounds causing the problems, developing simple analytical methods for the analysis of these compounds, providing advice to government agencies, university scientists and private consultants, and responding to occasional enquires from the public.

The taste and odor problems we have studied to date have been due to natural causes. Worldwide, the two most commonly reported natural taste and odor compounds are 2-methylisoborneol and geosmin. Most of our analytical effort has been focused on these two compounds.

RESEARCH RESULTS

During a severe taste and odor episode in the Edmonton water supply in March 1986, we analyzed several samples for geosmin and 2-methylisoborneol. This was done at the request of Professor S. Hrudey, University of Alberta, the consultant for the city. Geosmin was found in some of the samples, but the concentrations were too low to account for the severity of the problem. On the basis of this and other evidence, Professor Hrudey proposed that the problem was caused by low molecular weight aldehydes.

Since 1984, with Water Quality Branch, we have been collaborating with the Buffalo Pound Water Treatment Plant, which serves Regina and Moose Jaw. In the past they have experienced severe taste and odor problems in the summer due to dense blue-green algal blooms in Buffalo Pound Lake, which is the raw water source. In 1985, a granulated activated carbon (GAC) filtration unit went into operation at the plant for taste and odor removal. This was partly funded by the federal government. We provided baseline information on geosmin levels in 1984 prior to GAC treatment. In 1985, the plant began monitoring for geosmin using a method developed by us. Using this method they were able to show in 1986 that geosmin is released from algal cells at the pre-chlorination stage in treatment. Finished water concentrations can be three to four times as high as in the raw water. This may explain a similar observation in the Burlington water supply in the summer of 1983.

We completed our work with Alberta Environment on taste and odor problems in Lac St. Cyr, the water supply for St. Paul, Alberta. We were able to identify geosmin in some of the samples from the lake.

Some chloroanisole isomers cause a detectable odor at parts per trillion levels in water. Given the ubiquitous occurrence of chlorophenols in the environment and the possibility that they can undergo biological methylation to chloroanisoles, we decided to investigate this. We were able to find sub-ppt levels of some of the less potent isomers in a river and a well near the river. Given the low levels and the isomers found, however, they were not likely to cause a problem.

PUBLICATIONS

Brownlee, B.G. 1986. Analysis of taste and odour compounds in the Edmonton water supply, March, 1986. NWRI Contribution 86-77.

MacInnis, G.A. and Brownlee, B.G. 1987. Analysis of geosmin and 2-methylisoborneol in Lac St. Cyr—1986. Technical Note AED-87-1.

The Use of High Frequency Measurements in Water Quality Studies

B. Brownlee, Study Leader

G.A. MacInnis and A. El-Shaarawi

INTRODUCTION

Most water quality monitoring of rivers in Canada relies on monthly or less frequent sampling. Due to the dynamic nature of rivers, water quality studies for special purposes such as modelling require more frequent measurements. We have been investigating instrumentation for acquiring high frequency (hourly) measurements of basic water quality parameters such as temperature, dissolved oxygen, pH and conductivity. Because such instrumentation is capable of providing large quantities of data, we have also been working on statistical methods to analyze the results.

RESEARCH RESULTS

From 1982 to 1984, we acquired an extensive data base of hourly measurements of temperature, dissolved oxygen and pH in Canagagigue Creek as part of our studies on the dynamics of nutrients and organic contaminants in this creek. Preliminary analysis of the oxygen data by the method of Odum (1956) to calculate production, respiration and diffusion occasionally led to anomalous results due to the calculation method. Application of nonlinear regression techniques to one such set of results led to successful modelling of the dissolved oxygen changes. This provides an alternative to the classical method and a check on the results obtained by it.

Our 1982–84 measurements were made with standard field instruments. This was relatively inefficient due to the many difficulties encountered with the equipment. To alleviate this problem, two Hydrolab Datasondes were acquired in 1985 and have undergone extensive evaluation in our Calibration Laboratory. This is the subject of a report being prepared by J.S. Ford which describes the performance that can be expected from these instruments. During brief field tests in 1986, they were found to be easily deployed and recovered in a small creek. Their accuracy and precision is probably acceptable for most limnological studies. Our experience should be of interest to Water Quality Branch regions that have continuous monitoring programs.

A Terrachem water quality monitor was acquired in 1986. It is a lower cost alternative to the Hydrolab Datasondes. It will be put through a similar evaluation in 1987.

Our long-term interest has been the effect of nutrients, especially ammonium and nitrate, on the productivity of rivers. We can use commercial instruments such as the Hydrolab and Terrachem monitors to measure dissolved oxygen and calculate productivity, but no suitable instruments exist for high frequency measurement of nutrient concentrations. We have begun development work on an *in situ* monitor for ammonium using flow injection analysis. This monitor will be useful for our own water quality studies on rivers and for routine monitoring of rivers and lakes.

PUBLICATIONS

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Application of *In Situ* and Remote Optical Measurements to Aquatic Research

R.P. Bukata, Study Leader

J.E. Bruton, and J.H. Jerome

R.P. Bukata

INTRODUCTION

Radioactive transfer theory, which deals with the interactions of natural and artificial electromagnetic radiation with matter, has long been recognized as being an essential component of aquatic research since the life cycles of many organisms found in this environment are so intimately dependent on light.

RESEARCH RESULTS

During the past decade, NWRI has become proficient in the development and application of such radiative transfer models and methodologies. Current optical research includes three components, each of which is a combined blend of theoretical and experimental activities.

Multispectral Optical Monitoring System (MOMS)

The prototype of this in-house designed and fabricated monitoring system is ship-boom mounted and consists of a dual reflectance radiometer system. An upward-viewing subsystem is designed to record downwelling solar and sky irradiance. A downward-viewing subsystem is designed to record upwelling spectral radiance. Methodologies have been developed which enable the continuously recorded upwelling spectral radiance to be converted into subsurface volume reflectances. Through further radiative transfer modelling efforts, these spectral values of subsurface volume reflectance are related to organic and inorganic scattering and absorption components of the water mass being studied. MOMS has been successfully applied to a quasi-continuous monitoring of the suspended sediment concentrations in Lake St. Clair.

Digital Analyses and Display System (DADS)

This recently acquired digital image processing system has been rendered operational through the development of interpretation methodology software. This past year has seen DADS applied to sediment transport through the Upper Great Lakes connecting channels, plume dynamics and upwelling phenomena in the Niagara River/Lake Ontario area, marshland delineations along Lake St. Clair, and water quality aspects of Hamilton Harbour. The sources of remotely acquired data used in DADS include the LANDSAT series of satellites, the NOAA series of satellites and NIMBUS-7. Airborne multispectral data have also been recently obtained for future use with DADS.

Optical Modelling and Special Projects.

This aspect of the research effort has resulted in the development of a conceptual mathematical model which describes the impact of persistent changes in ambient water levels on the areal extent (as delineated in remote synoptic overviews) of shoreline marshes.

An additional study was initiated jointly with the Water Quality Branch, Pacific and Yukon Region, to evaluate water color perception in British Columbia rivers. *In situ* measurements of subsurface spectral irradiance were performed in a dozen rivers including the Fraser, Thompson and Columbia. These data are currently being evaluated.

Environmental Simulation/ Statistical Data Analysis

A.H. El-Shaarawi, Study Leader

A.H. El-Shaarawi
(Photograph unavailable)

INTRODUCTION

The goals of the study are to develop appropriate statistical techniques for collecting water quality data in such a way that valid inductive inferences may be drawn from them, and for extracting the maximum amount of information from existing environmental data in the most efficient way.

RESEARCH RESULTS

1. Several techniques for the estimation of loadings were evaluated mathematically and empirically by simulation. The results show that numerical integration methods are superior to the finite population approach or the ratio method.

2. A new technique was developed for dealing with data below detection limit.

3. A new technique was developed for estimating the number of samples needed to detect differences in the concentrations of a toxic substance at the head and mouth of the Niagara River.

PUBLICATIONS

El-Shaarawi, A.H. and Kiwatbowski, R.E. eds. Statistical aspects of water quality monitoring. Developments in water science, vol. 27, Elsevier, Amsterdam.

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El-Shaarawi, A.H. and Pipes, W.O. 1986. Statistical inferences about the ratios of bacterial densities. Water Res. In press.

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El-Shaarawi, A.H. 1986. Statistical aspects of setting a sampling strategy. J. français d'hydrologie 17: 37–46.

Mackenzie River Program

E.D. Ongley, Study Leader

J.H. Carey and E. Nagy

E.D. Ongley

INTRODUCTION

The Mackenzie River program arises from a series of issues identified by Northern Programs Office-Inland Waters/Lands, Yellowknife. The first arises from a growing concern over apparent deterioration of fish stock in the lower Mackenzie River. Although the cause was not apparent, there was concern that changes in oil seeps into the bed of the Mackenzie River arising from artificial island construction in the early 1980s in the Norman Wells area might be resulting in larger quantities of hydrocarbons released into the aquatic environment.

A second issue relates to the generally low level of understanding of chemical transport in northern aquatic systems and the attendant problem of cost-effective environmental sensing of such large systems. In the Mackenzie system, chemicals which might be expected to be transported into the Beaufort Sea are: agricultural chemicals from the Peace River District; heavy metals from mining operations in the Mackenzie Mountains; toxic chemicals such as cyanide released as part of ore treatment; and hydrocarbons from oil and gas exploration and extraction in the Mackenzie basin and its major tributary, the Liard. This research addresses the specific concern of presence and pathways of hydrocarbons in the main stem of the Mackenzie River and, secondarily, the development of more efficient monitoring protocols for environmental sensing in northern aquatic system.

RESEARCH RESULTS

With field staff from the National Hydrology Research Institute (NHRI) Saskatoon, two cruises down the main stem of the Mackenzie River were carried out, one during late summer low flow in 1985 and the second during high flow immediately following ice breakup in 1986. Our work elsewhere indicates that chemical pathways are profoundly differentiated by contrasting extreme flow regimes. The Mackenzie was sampled at seven sites over some 1350 km, from Fort Simpson to Inuvik. Also sampled was the mouth of the Liard River, the major tributary of the Mackenzie and source of most of the suspended sediment in the upper Mackenzie. Water and suspended sediment were sampled, the latter by a Sedisamp continous-flow centrifuge. Bottom samples were not generally possible due to the coarse nature of the bed materials. Water and suspended sediment samples were analyzed for nine metals by staff of NHRI. After normalization for particle-size differences, metal data will provide an indicator of water and sediment partitioning and of chemical enrichment and downstream change necessary for establishing baseline values for future monitoring. Future work includes fractionation of sediment-associated metals as an index of bioavailability.

Suspended sediment for hydrocarbon analysis was frozen in the field in acetone-cleaned aluminum foil. Clarified water (18 L) was trickle filtered under pressure through an SAC-2 resin column to capture water-soluble organics. The water samples were solvent extracted by acetone/hexane into neutral and acid fractions; the sediment samples were extracted by acetone/hexane into an acid fraction and four base/neutral fractions. Part of the sediment extracts were exchanged in DMSO and bioassayed for developmental, genotoxic and lethal effects on the nematode *P. redivivus*.

The June 1986 high flow samples found higher alkane and polyaromatic hydrocarbon (PAH) than the previous low flow survey in August of 1985. The concentration distributions along the river suggest diffuse inputs of these organics by spring runoff from the drainage basin; this overwhelms any inputs from the refinery at Norman Wells or from channel-bottom oil seeps. Presence of diffuse sources suggests that atmospheric transport of organic compounds into the Mackenzie basin are making an appearance in river water. The distribution of the organics between the suspended sediments and the water phase show the need for analyzing both phases for estimates of organic loadings in the river.

PUBLICATIONS

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Contaminants/Pesticides

R.J. Maguire, Project Chief

R.J. Maguire

Initial concern about the threat posed by persistent toxic substances to human health and the aquatic ecosystem were raised in the 1960s with regard to the use of certain pesticides and their undesirable persistence in the environment. The number of chemicals in use in North America has expanded drastically over the past fifty years. Today about 70,000 chemicals are produced or used in North America, including several hundred pesticides. The fact that some chemicals have produced cancers in humans, tumours and deformities in fish, plus a wide range of other detrimental human and environmental problems has heightened public concern about the hazards of chemicals generally. Some of the chemicals present in the environment are known to produce detrimental effects at the concentrations encountered in the environment. Many of these are already subject to regulatory control. Other chemicals are known to produce detrimental effects at elevated concentrations, but little or no information is available regarding effects which may occur at the low concentrations encountered in the environment.

The aim of the Contaminants/Pesticides Project is to generate information on the nature, extent and effects of contamination of Canadian rivers. This information will be used in the evaluation of hazards of chemicals as mandated by the Environmental Contaminants Act and the Pest Control Products Act. The information will also be used for the establishment of water quality guidelines and standards.

The hazard posed by a toxic substance to an organism in any medium such as water or sediment is a function of its toxicity and its concentration and persistence in water or sediment. In general, the approach followed in attaining the project objective for any given chemical involves (i) establishing methods of analysis for relevant media; (ii) determining the environmental occurrence of the chemical; (iii) determining the persistence and fate of the chemical in the relevant aquatic compartments (such as water, sediment, biota, etc.) from the point of view of physical, chemical and biological removal mechanisms, and (iv) determining the effects of the chemical on aquatic organisms, communities and ecosystems.

SHORT-TERM OBJECTIVES

1. Carry out field and laboratory research on nature, pathways and biological effects of target inorganic and organic contaminants. Initially field programs will focus mainly on the Yamaska River, Quebec; during 1987/88 a coordinated plan of research will be developed with Agriculture Canada for pesticides in selected watersheds in Southern Ontario.

2. Participate with the Water Quality Branch and the Commercial Chemical Branch to deliver Conservation and Protection's responsibilities under the Pest Control Products Act and the Environmental Contaminants Act.

3. Provide expert advice to a range of clients on a demand basis.

Fate of Industrial Organic Compounds and Pesticides in Water

R.J. Maguire, Study Leader

R.J. Tkacz

INTRODUCTION

This new study was begun in 1986/87. There are three aspects of the study.

Fate of Deltamethrin Sprayed on a Pond and Stream in P.E.I.

The photostable pyrethroids, of which deltamethrin is one, are a relatively new class of pesticides which are notable for their high toxicity to insects and low mammalian toxicity. They have potential large-scale use in agriculture and forestry. Pyrethroids are fairly toxic to aquatic insects and, indirectly, to organisms which feed upon such insects. For this reason, pyrethroid use is normally restricted to certain areas removed from streams or ponds. As part of a joint National Water Research Institute- Environmental Protection Service, Atlantic Region-Water Quality Branch, Atlantic Region study on the effects of deltamethrin on aquatic biota, we examined the persistence and fate of deltamethrin in a pond and stream after a direct overspray by collecting samples of subsurface water, surface microlayer, suspended solids, sediment and benthic invertebrates. We are currently analyzing these samples for deltamethrin and four of its likely degradation products.

Loading of Toxic Chemicals to Lake Ontario from the Surface Microlayer of the Niagara River

The surface microlayer of natural waters is a thin film of natural and anthropogenic surface-active material. We and others have shown that toxic chemicals can accumulate in surface microlayers relative to subsurface water. Concentrations of some contaminants in the surface microlayer are occasionally so high that the amount of a particular chemical in the microlayer is greater than the amount in the whole depth of subsurface water. This fact has been largely unrecognized previously and may, for example, necessitate revisions of estimates of loadings of toxic substances from the Niagara River to Lake Ontario. Because of turbulence, however, concentrations of toxic substances in surface microlayers are expected to be fairly variable with time. In this new study, we wanted to study the temporal variability of such concentrations. We collected samples of subsurface water (20 L) and surface microlayer (4 L) from the Niagara River at Niagara-on-the-Lake at weekly intervals for one year. The aim was (i) to compare concentrations of polychlorinated biphenyls, organochlorine pesticides and chlorobenzenes in the two "compartments" with time; (ii) to compare the distribution of such chemicals between suspended solids and water in each compartment, and (iii) to check the samples for the presence of certain nitrogen-containing industrial chemicals (cf. Yamaska study below).

Fate of Amines and Pesticides in the Yamaska River, Quebec

The Yamaska River basin is a relatively small (4900 km^3) river basin in the Eastern Townships of Quebec, about 70 km east of Montreal. Major towns in the Yamaska basin are St-Hyacinthe, Granby, Cowansville, Farnham and Acton Vale. More than one quarter of all pesticides used for agricultural purposes in Quebec are used in this river basin, encompassing virtually all classes of pesticides. The major classes of pesticides are triazines and triazoles, amides, carbamates and organophosphates. It is the purpose of this study to identify those pesticides which are getting into the water, to determine their mode of transport and their loading to the St. Lawrence River, to determine their persistence and fate in water and sediment, and eventually to determine their effects on aquatic biota. In addition, we have similar aims for industrial chemicals used in the Yamaska basin, in particular nitrogen-containing chemicals and dyestuffs (since the Eastern Townships are the heart of Canada's textile industry and there are 11 fabric mills and associated dyeing operations on the Yamaska). The Yamaska River offers the opportunity to separate some effects since there are areas of exclusive agricultural activity, areas of exclusive industrial activity, and areas in which there are both agricultural and industrial activity.

RESEARCH RESULTS

Fate of Deltamethrin Sprayed on a Pond and Stream in P.E.I.

Results to date indicate that deltamethrin disappears from the surface microlayer very quickly, with a half-life of five minutes. It also disappears from subsurface water fairly quickly, with a half-life of about 45 minutes. In both cases we found small amounts of metabolites. We did not find deltamethrin in the sediments. In addition to completing our analyses, we are investigating the sunlight photochemical degradation of deltamethrin on soil surfaces, and the relative importance of volatilization of deltamethrin from the surface microlayer and from the subsurface of natural waters.

Loading of Toxic Chemicals to Lake Ontario from the Surface Microlayer of the Niagara River

Sample collection was completed in the fall of 1986. The samples are presently being analyzed.

Fate of Amines and Pesticides in the Yamaska River, Quebec

The first part of this study was conducted in the summer of 1986. Samples of subsurface water, surface microlayer, suspended solids, sediment, fish and benthic invertebrates were collected from 20 locations along the length of the Yamaska River. These samples are currently being analyzed. We have completed the Microtox, fecal coliform and volatile chemical analyses on the samples collected in 1986. These preliminary results indicate that Granby and St-Hyacinthe are "pollution hot spots" on the river. Remaining are analyses of water, sediment, fish and benthic invertebrates for pesticides and some industrial chemicals. When the identification stage of our work is finished, we will choose pesticides and other chemicals upon which to concentrate our efforts in determining persistence, fate and effects.

PUBLICATIONS

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Biomonitoring Techniques for Pesticides in Aquatic Systems

J.L. Metcalfe, Study Leader

S.P. Batchelor, A. Mudroch and J. Merriman (Water Quality Branch-Ontario Region)

J.L. Metcalfe

INTRODUCTION

The Water Quality Branch of the Inland Waters/Lands Directorate (IW/LD) has requested the development of biomonitoring techniques for water quality assessment. Biomonitors can be used as a screening tool for the early detection of environmental contaminants and for subsequent trend monitoring. Biomonitors also provide a measure of the bioavailability of contaminants and a means of assessing their toxic effects at the organism and community levels. This study consists of five investigations, each addressing one or more aspects of biomonitoring research.

RESEARCH RESULTS

Shubenacadie Lakes Biomonitoring Study

The Shubenacadie Lakes in Nova Scotia are contaminated with arsenic (As) and mercury (Hg) as a result of past gold mining activities in the area. In earlier work, we reported very high concentrations of both elements in macroinvertebrates from the most contaminated lakes. Further research identified chironomids as suitable biomonitors for the profundal zones based on the excellent correlation between As and Hg concentrations in the sediment and in their tissues. Because of their high bioconcentration capacities for As and Hg, respectively, we also recommend the snail, *Helisoma* sp. and the mussel *Elliptio complanata* as biomonitors for the littoral zones. Concentrations of Hg in *E. complanata* were found to increase almost exponentially with increasing organism size, prompting us to investigate the influence of age on the bioaccumulation process in mussels. We found that *E. complanata* could be aged much more accurately than the other two mussel species with which it co-exists, and that it lived twice as long (20 vs. 10 years). As a result, age classes may be analyzed separately and age/contaminant relationships evaluated most confidently for this species. Furthermore, *E. complanata* from the most contaminated lake were significantly smaller at a given age than those from a less contaminated lake, suggesting the possibility of a stress response. We recommend *E. complanata* for biomonitoring in the Atlantic region.

Ottawa River Biomonitoring Study

The goal of this study is to develop a biomonitoring program for the Ottawa River. In the first year, we found mussels to be excellent candidates. Two species, *Lampsilis radiata* and *E. complanata*, were abundant throughout the system, bioaccumulated high concentrations of heavy metals, and provided information on bioavailability not apparent from sediment analysis alone. Elevated levels of As, Cd and Hg were identified, and metals were more bioavailable at Treadwell, downstream of the South Nation River, than at Castleford, upstream of Ottawa. In 1986, samples were again collected at Treadwell and also at Carillon, which represents the transboundary site between Ontario and Quebec and the deposition zone at the mouth of the river. Concentrations of metals in sediment were highest at Carillon; Environment Quebec's sediment quality criteria were exceeded for As, Cd and Zn at both sites and for Hg in *E. complanata* at Treadwell. Mercury concentrations were an order of magnitude higher in *E. complanata* from Treadwell (1.3 μg/g) than from Castleford (0.15 μg/g) or Carillon (0.21 μg/g) despite similar concentrations in the sediment throughout (0.11, 0.13 and 0.13 μg/g, respectively), suggesting that Hg is more bioavailable at Treadwell. Hepta- and octachlorodibenzo-p-dioxins were also found in sediment and mussels at Treadwell, but not at Castleford. Therefore, Treadwell may be a sensitive location for a biomonitoring station. Mussels are currently being scanned for other organic contaminants. Also, *E. complanata* exposed for two months at 11 sites in the lower river in 1986 will be analyzed for organic contaminants, with emphasis on pesticides in the vicinity of the South Nation River.

Yamaska River Biomonitoring Study

An investigation into biomonitoring techniques suitable for pesticides and industrial chemicals in the

Yamaska River was begun. Caged mussels, *E. complanata*, were exposed for periods throughout the growing season in each of five tributaries known to be contaminated with agricultural pesticides. Mussels are expected to be good biomonitors for pesticides because their elimination rates for xenobiotics are slow. Also, because they can survive lengthy exposures, stress responses indicative of local environmental conditions may develop. Samples are awaiting analysis for pesticide residues and physiological indicators of stress. In addition, the health of the benthic invertebrate community was assessed at six strategic locations. From preliminary results, it is apparent that community structure varies greatly with type and degree of pollution. The two sites influenced only by light industry or farming had diverse communities (23-31 taxa) including pollution-sensitive mayflies, stoneflies, caddisflies and beetles. Another site, downstream of a source of metals, also had a diverse community (30 taxa), but stoneflies were conspicuously absent. At a fourth site downstream of a village with a textile mill, the community was moderately diverse (21 taxa), but the absence of case-dwelling caddisfly larvae and the abundance of oligochaetes indicated nutrient enrichment. The last two sites, downstream of major industrial centers, were severely degraded. Only 10-11 taxa were present, and pollution-tolerant annelids and Diptera dominated. Further research aimed at identifying the benthic communities representative of various types and degrees of pollution (pesticides, municipal discharges, industrial chemicals) is planned.

Rainy River Biomonitoring Study

A joint study with the Ontario Ministry of the Environment (MOE) to compare the leech, *Nephelopsis obscura*, and the mussel, *E. complanata*, as biomonitors for chlorophenols and dioxins in the Rainy River was undertaken. In past work, MOE found mussels to be unsatisfactory for detecting chlorophenols in the environment. In contrast, our previous work with leeches showed that these organisms bioaccumulate chlorophenols to very high levels. Cages of leeches and mussels were exposed together for three weeks at 17 sites along the river. Samples have been submitted for analysis of chlorophenol and dioxin residues. Leech caging experiments were found to be feasible, with at least 80% survival under suitable water quality conditions.

Early Development of the Common Shiner, *Notropis cornutus*

There is virtually no published information on the early life history of this common forage fish. The purpose of our study was to provide this information, by means of detailed descriptions and illustrations, enabling field workers to separate larval and juvenile common shiners from other minnows. As our report describes the *normal* early development of the common shiner, it will be valuable to toxicologists interested in testing the effects of environmental contaminants on the sensitive early life stages of this native species.

PUBLICATIONS

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Fate and Effects of Metals in Contaminated Areas

Y.K. Chau, Study Leader

G.A. Bengert and P.T.S. Wong (Great Lakes Laboratory for Fisheries and Aquatic Sciences)

Y.K. Chau

INTRODUCTION

Molecular tetraalkyllead species and ionic trialkyllead, dialkyllead species (Me,Et) have been found in a variety of environmental samples, including surface microlayers, fish, sediments and aquatic plants in the St. Clair and St. Lawrence rivers near several lead alkyl production plants. Because these compounds are highly toxic, their occurrences have necessitated investigations to understand their bioaccumulation and fate in biota and in the aquatic system.

Adenylate energy charge (AEC) is a calculated ratio based on the concentrations of adenine nucleotides (AMP, ADP, ATP) in the biota. It is a biochemical indicator of the physiological activity of an organism. Any factors which upset the metabolic processes of an organism will be reflected in changes in the AEC values. Thus, the AEC can be developed into a sensitive, quantitative and comprehensive parameter for use in the biomonitoring of environmental stress and in measuring toxic effects.

RESEARCH RESULTS

Caged clams (*Elliptio complanata*) experiments were carried out in the St. Clair and St. Lawrence rivers to investigate the bioconcentration of alkyllead compounds. Three to four stations were set up, each about 1 km apart downstream from the source. Results obtained in two years (1985-86) indicated that:

1. No alkyllead compounds were detected in clams at the control site, which is several kilometres upstream of the production plants.

2. The alkyllead compounds found in environmental samples, water, sediment, plant, fish were mainly tetraethyllead and its degradation products, namely, triethyllead, diethyllead and Pb(II). The highest concentration of alkyllead species in the exposed clam was found in the viscera, followed by gills and mantle tissues.

3. In the St. Clair River, the highest concentration of alkyllead in whole clams was found at site No. 2, 0.7 km downstream of Ethyl Corporation; the concentration decreased as the distance from Ethyl Corporation increased, indicating the point-source nature of the alkyllead emission from the production plant. Similar phenomena were observed in the St. Lawrence River off Maitland where DuPont Co. is located.

4. Total alkyllead concentrations in whole clams increased with exposure time (June to September). The highest concentration of total alkyllead, 156 ng/g, was found in a clam in September in the St. Clair River at site No. 2, and 126 ng/g was found in August in a clam in the St. Lawrence River at No. 1.

5. The source of trialkyllead and dialkyllead in clams was probably derived from direct intake from water. We could not, however, produce definitive proof to indicate the *in vivo* degradation of tetraalkyllead to trialkyllead and dialkyllead inside the clam, although such reactions have been proposed.

6. The highest concentration of alkyllead in clams was the triethyllead species (98-103 ng/g), indicating its *in vivo* stability in clams. The concentration of the diethyllead species was generally very low or at trace levels.

7. Tetraethyllead was never detected in water at any of these sites. The reasons are probably due to its volatility which makes its water residence transient, and due to its fast degradation in the presence of light. Triethyllead and diethyllead were frequently detected in water and the surface microlayer. The highest concentration of diethyllead in water was in September, suggesting the photolytic degradation of tetraethyllead to triethyllead and to diethyllead by the in-

tense sunlight. Pb(II) was also high in these samples.

8. No clam was killed in the course of the three-month exposure experiment.

9. Parallel clam exposure experiments were carried out using aquaria in the laboratory under controlled conditions. Contaminated sediments from the same locations were used. Three clams were removed from the exposure aquaria for analyses at weekly intervals to follow the bioaccumulation and depuration rates. The results obtained in these experiments will be compared with that obtained in the field. Data evaluation is still in progress.

10. A sensitive HPLC technique has been developed for measuring the adenine nucleotides (AMP, ADP, ATP) for the calculation of AEC in algae. It is an isocratic elution technique using phosphate buffer as an eluant in a C-18 reversed phase column, with detection limits at the picomole level. The technique will be applied to the study and evaluation of environmental stress in several areas, e.g., St. Clair, St. Lawrence, Yamaska rivers, etc., during the summer.

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Ecotoxicological Study on Contaminant Biodegradation in Fluvial System

D. Liu, Study Leader

K. Thomson, Y.K. Chau and B.J. Dutka

D. Liu

INTRODUCTION

Biodegradation is one of the major processes for the elimination of a contaminant from the aquatic ecosystem. This important process is strongly influenced by many factors, such as the availability of organic and inorganic nutrients to the microbiota, temperature, dissolved oxygen, and the oxidation-reduction potential of the aquatic compartment. Because of the many variables involved in this degradation process, it is often impossible to accurately elucidate the biodegradation mechanism and metabolic pathways involved in the removal of a contaminant in a natural environment. Therefore, a river modelling system is being developed in our laboratory in order to assess the fate and persistence of contaminants and pesticides, which have been identified as priority chemicals having a significant impact on the health of aquatic ecosystem. One of the major roles of our laboratory in Rivers Research Branch (RRB), is to provide an answer to or to resolve some of the puzzles observed during field work. For instance the pesticide, fenitrothion, used in the spruce budworm control program on the east coast, was found to have a tendency to partition into the sediment and rapidly disappear. Our laboratory investigation demonstrated that this pesticide is far more susceptible to co-metabolism degradation under anaerobic conditions, i.e., organic matter in sediment could speed up its biodegradation. We are fully convinced that the RRB's integrated approach to contaminant/pesticide management, combining both field and laboratory studies, is the most efficient and appropriate way to resolve the difficult problem of toxic chemicals.

RESEARCH RESULTS

Toxicity assessment is one of the few important parameters commonly used in the characterization of a chemical's behavior in the environment. This assessment is now also required as an integral part of the hazardous evaluation of new chemicals in the toxic substances legislation testing scheme of many countries. For example, the Organization for Economic Cooperation and Development (OECD) has issued a series of test guidelines on performing toxicity assessment of chemical compounds. However, some technical difficulties are still frequently encountered in conducting aquatic toxicity tests. One of these is the insolubility of many chemicals in water, which impedes the determination of acute and sublethal toxicity levels of these chemicals. Now we have successfully overcome this difficulty by the development of a refined resazurin reduction method by which the toxicity of both water soluble and insoluble compounds can be easily and directly assessed. To assist in the technology transfer to industries and other government agencies, the resazurin reduction method for toxicity assessment has also been prepared in a step-by-step cookbook format, so that most laboratory staff are able to perform the toxicity test without the need for further reference. The potential and usefulness of the refined resazurin reduction test in environmental toxicology research are clearly demonstrated in the Quantitative-Structure-Activity-Relationships (QSAR) study of chlorobenzenes and alkyltins. The results indicated that molecular geometry and electronic properties could be very important in eliciting a toxicant's biological activity.

Biodegradation is one of the prime processes affecting a contaminant's persistence, fate and behavior in the aquatic environment. Consequently, the study of the biodegradation processes of contaminants, particularly those of water-insoluble compounds, will result in a better understanding of why some chemicals are more persistent than others. The information obtained from such a study may lead to better management of toxic substances in the environment. In this regard, an extensive review covering biodegradation mechanisms, processes, kinetics and laboratory procedures has been delineated in one of our publications.

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Effects of Dissolved Organic Matter on the Bioaccumulation of Synthetic Pyrethroids by Zooplankton

K.E. Day, Study Leader

D.R.S. Lean

K.E. Day

INTRODUCTION

The synthetic pyrethroids, e.g., permethrin, cypermethrin, deltamethrin and fenvalerate, are a group of insecticides currently registered and widely used on many agricultural crops in Canada. As a group, the pyrethroids are classified as moderately persistent, hydrophobic chemicals with low mammalian toxicity but high toxicity to fish and many aquatic invertebrates. The accidental introduction of the synthetic pyrethroids into the aquatic environment through overspray, drift or runoff may result in these chemicals becoming quickly adsorbed to living and non-living particulate matter and/or colloidal or dissolved organic matter. It is unknown whether or not such adsorbed chemicals are bioavailable to aquatic organisms either to exert a toxic effect or to bioaccumulate or both. This study was initiated to examine the effects of dissolved humic material (DHM) on the bioavailability and bioaccumulation of several synthetic pyrethroids to the cladoceran, *Daphnia magna*.

RESEARCH RESULTS

The presence of DHM in water increased the surface area available for adsorption of the hydrophobic pyrethroids, deltamethrin, fenvalerate and cyhalothrin. This was shown indirectly by determining the amount of pesticide found to adsorb to the sides of the glass bioassay beakers and the amount of radiolabelled pesticide present in the water.

The binding of the synthetic pyrethroids to DHM directly affected the accumulation of these chemicals by *D. magna*. The percent of the applied radioactivity found in the animals decreased from 2.7% to 0.4% for deltamethrin, 3.1% to 0.6% for fenvalerate and 3.8% to 0.5% for cyhalothrin as DHM increased. The amount of actual chemical in the bodies of the animals decreased from 0.31 to 0.04 pmole deltamethrin/gram wet weight, 3.40 to 0.72 pmole fenvalerate/gram wet weight, and 1.55 to 0.22 pmole cyhalothrin/gram wet weight. These results suggest that a contaminant bound to DHM greatly reduces the bioavailability for uptake by organisms compared to unbound contaminants.

PUBLICATIONS

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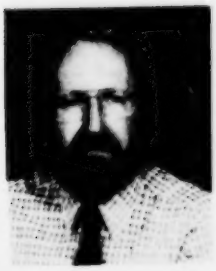
Groundwater Contamination

R.E. Jackson, Project Chief



R.E. Jackson

ISSUE AND RATIONALE

Groundwater pollution, arising from waste-disposal sites and pesticide application, can cause the contamination not only of wells but also of surface waters such as the Great Lakes system.

In eastern Canada, groundwaters are particularly important in supplying municipal, agricultural and industrial needs in southern Ontario, the St. Lawrence valley and the Maritime provinces. Aquifers, the groundwater reservoirs satisfying these needs, are threatened with contamination by pesticide and fertilizer residues and industrial and municipal wastes.

However, it is the migration of groundwater contamination from dump sites and landfills through fractures in rocks and its subsequent discharge to the rivers and lakes of the Great Lakes system that has aroused the most concern in recent years. In its 1985 report to the International Joint Commission (IJC), the Great Lakes Water Quality Board called for "programs to establish the impact of contaminated groundwater on the surface waters of the Great Lakes Basin ecosystem." The IJC, in its second biennial report in 1984, called for research into groundwater sampling and the development of protocols for the monitoring of toxic waste sites. Programs based on these recommendations form the basis of the NWRI groundwater contamination project.

Long-Term Strategic Goal

By undertaking field, computational and laboratory studies to examine the migration and fate of toxic contaminants in the subsurface, expertise in contaminant hydrogeology is created. Benefits derived include the development of guidelines for waste site assessment and remedial measures for aquifer restoration.

Types of Activities

The research program is focused on the migration and fate of toxic contaminants in groundwater at several field study sites which have been instrumented with monitoring systems installed in drilled boreholes. The field sites provide the data which is analyzed with the help of laboratory experiments and mathematical models at NWRI. The research program is comprised of several studies which are outlined below with the locations of the field study sites listed in parentheses:

No. 83041: hydrogeology of the Niagara frontier (Navy Island);
No. 83042: hydrogeology of the St. Clair River Valley (Sarnia);
No. 83043: predicting the migration of dense non-aqueous phase liquids in fractured rocks (laboratory experimentation);
No. 83044: toxic chemicals in groundwater (Gloucester landfill and Chalk River radioactive waste area);
No. 83045: pesticide migration and fate in groundwater (P.E.I.).

Project Objectives

There are three general objectives. The first is to understand the physical and chemical controls on contaminant migration and fate in sedimentary rock aquifers, such as the limestones of the Niagara region, which are contaminated with liquid industrial wastes, or the sandstones of P.E.I., which are contaminated with pesticides. The second is to develop and/or apply operational tools for hazardous-waste site assessment and aquifer restoration, such as groundwater sampling protocols and computer codes to determine the optimum decontamination of an aquifer. The final objective is to draw upon the expertise developed in pursuit of the first two objectives to give advice on groundwater pollution matters of federal concern in eastern Canada.

Performance Indicators

Journal papers, on the following topics, will be submitted and/or published during 1987/88:

- hydraulic testing of fractured rocks along the Niagara River;
- groundwater velocities beneath Chemical Valley, Sarnia;
- radionuclide sorption by aquifer sediments at Chalk River;
- pesticide migration and fate in the sandstone aquifer of P.E.I.;
- field testing of contaminant tracer migration in rock;
- review of methods for the analysis of aldicarb.

Migration and Fate of Aldicarb in the Sandstone Aquifer of Prince Edward Island

R.E. Jackson, Study Leader

S. Lesage, K.S. Novakowski and M.W. Priddle

INTRODUCTION

Pesticide contamination of groundwater is an environmental and public health concern throughout Canada, particularly in the Maritime provinces where groundwater is a major source of water for all uses, e.g., food processing, drinking, etc. Surveys of farm wells on Prince Edward Island (P.E.I.) between 1983 and 1986 indicated that low levels (1-5 μg/L) of the toxic insecticide aldicarb were present in 18% of high risk wells. Such contamination frequently occurs under conditions in which soluble, persistent pesticides are applied to crops grown on sandy soils. This study concerns the migration and fate of aldicarb in groundwater at NWRI's field sites on P.E.I. where this insecticide is used on potatoes.

Aldicarb is an extremely toxic carbamate insecticide (LD_{50} = 0.9 mg/kg) with a solubility of 0.6% and a hydrolysis half-life of 10-650 weeks. Because of its toxicity, aldicarb is applied in granular form during spring seeding. The granules dissolve and the insecticide undergoes rapid microbially catalysed oxidation to the sulfoxide, which, in turn, undergoes either hydrolysis to relatively nontoxic oximes or oxidation to the toxic sulfone and then similar hydrolytic degradation. Health and Welfare Canada recommends a maximum concentration of 9 μg/L for total aldicarb.

RESEARCH RESULTS

The Field Study Sites

The NWRI sites are the McCardle Farm, near Augustine Cove, which is operated by Eric Robinson Inc., and fields at Mill Valley and New Annan, near Kensington, owned by Cavendish Farms Ltd. These sites were chosen because the input of pesticides and fertilizers to each field over the past few years is well-documented. For instance, at Augustine Cove approximately 2 kg aldicarb/hectare were applied in 1983 and 1986, in which years approximately 200 kg N/ha were also applied in the form of ammonium nitrate fertilizer.

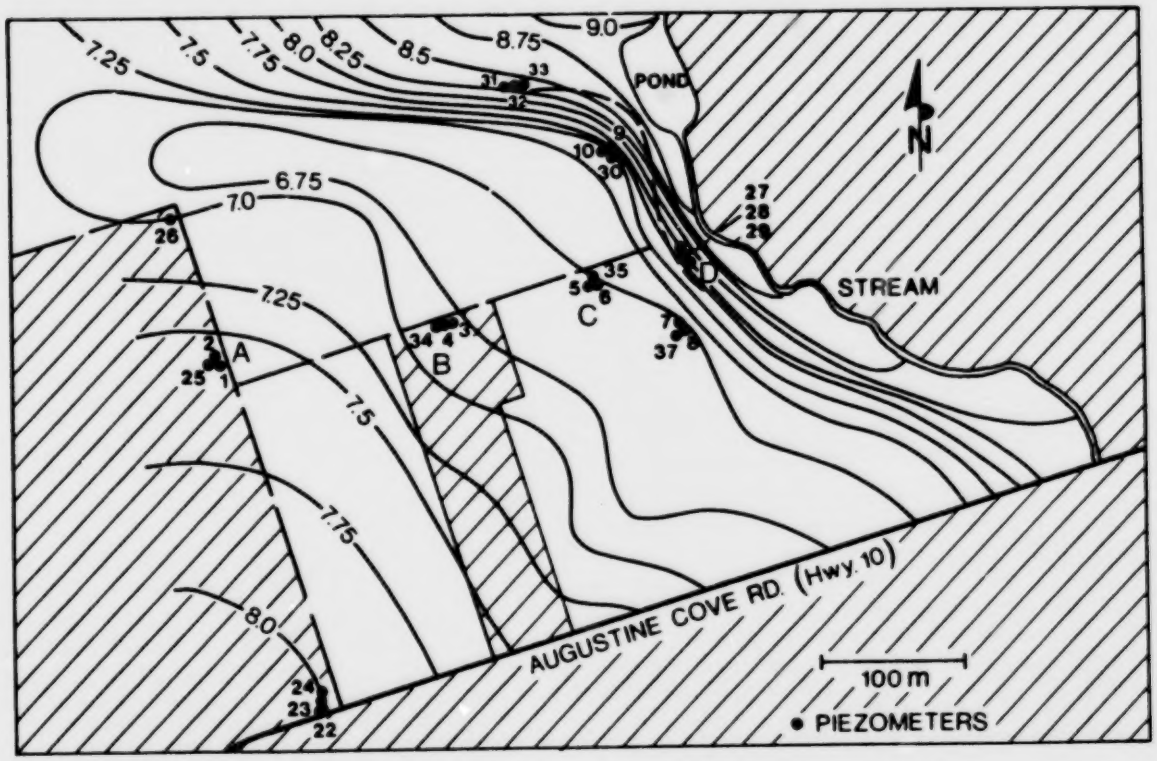


Figure 3a. Water table contours in metres above mean sea level, Augustine Cove, P.E.I., September 1986.

All sites were established in the main potato growing area of P.E.I., i.e., eastern Prince County. The hydrostratigraphy consists of 2-3 m of silty fine sand underlain by fractured fine-grained sandstone. In 1985, the sites were instrumented by installing 10 piezometers (5-cm inside diameter, schedule 40 PVC with a 1- or 2- m long No. 6 slot PVC screen) using an air rotary drilling rig. The piezometers were installed in pairs with the screen of the shallow piezometer set to intercept the water table; the deeper screen was set about 6 m below the water table. These piezometer pairs were oriented in a T-shaped pattern with the foot of the T at the topographic high point of the field; three pairs of piezometers are distributed along the lowest contour line in the field. In 1986, the Augustine Cove site was more heavily instrumented with the addition of three nests of three piezometers. A further six single wells were installed in an attempt to just intersect the water table. These piezometers are shown in Figure 3 in both plan (Fig. 3a) and cross-sectional (Fig. 3b) views. The rest of this report shall only concern this particular site, for which the results are the most complete.

During 1986, seven piezometers at Augustine Cove were slug-tested with the aid of a pressure transducer to determine hydraulic conductivity. The values of hydraulic conductivity measured ranged from 2×10^{-4} to 5×10^{-6}, with a mean value of 8.5×10^{-5} m/s. The responses of piezometers 1, 3 and 27 reflect semi-confined conditions at depth in the sandstone aquifer, probably due to the siltstone aquitard shown in Figure 3b.

Groundwater Quality in the Sandstone Aquifer

Groundwaters were analyzed potentiometrically in the field for pH, EH, O_2, NH_3 and electrical conductivity. Samples were collected with a Teflon bladder pump (Well Wizard, QED Systems, Ann Arbor, Michigan). Aldicarb samples were filtered, acidified to pH 5 and stored at 4°C prior to analysis, which was conducted using the method of Chaput (1986). Results of the analyses for Augustine Cove are shown in Table 2, except for the inorganic analytes which are not reported here.

Table 2. Groundwater Chemistry, Augustine Cove, September 1986

	Chemical Parameter						
Piezometer	pH	E_H Volts	O_2 mg/L	NO3-N mg/L	HCO_3 mg/L	Total Aldicarb µg/L	Sulfone/ Sulfoxide
1	7.6	0.43	8.7	8.4	104	0.42	1.66
2	7.0	0.49	9.2	8.1	70	0.68	1.40
3	8.2	0.39	7.8	1.9	109	n.d.	-
4	7.0	0.43	8.7	7.6	101	3.60	2.11
34	7.0	0.43	8.1	8.4	101	4.2	2.07
5	6.9	0.14	0.2	<0.05	120	n.d.	-
6	6.4	0.42	5.7	8.4	49	7.10	3.19
27	6.8	0.13	0.3	<0.05	207	n.d.	-
28	6.3	0.33	0.4	1.2	124	1.00	10.0

n.d. - not detectable;
- - not measured.

All aldicarb detected at Augustine Cove was either in the sulfoxide or sulfone form. The ratio of sulfone to sulfoxide has increased over the 15-month period that measurements have been made. The mean value at six piezometers has increased from 1.8 in July, 1985 to 2.4 in September 1986. In general, it seems that the sulfone:sulfoxide ratio is < 1.0 up to 12 months after application and is > 2.0 two years after application.

Table 2 shows that there is a correlation between total aldicarb and groundwater pH. Total aldicarb tends to increase down the flow system while, in an anomalous manner for groundwater flow systems, the pH decreases down the system. The analyses also indicate that the aldicarb concentrations are the highest where the water table is the shallowest. This likely reflects the distance in the unsaturated zone through which the aldicarb must

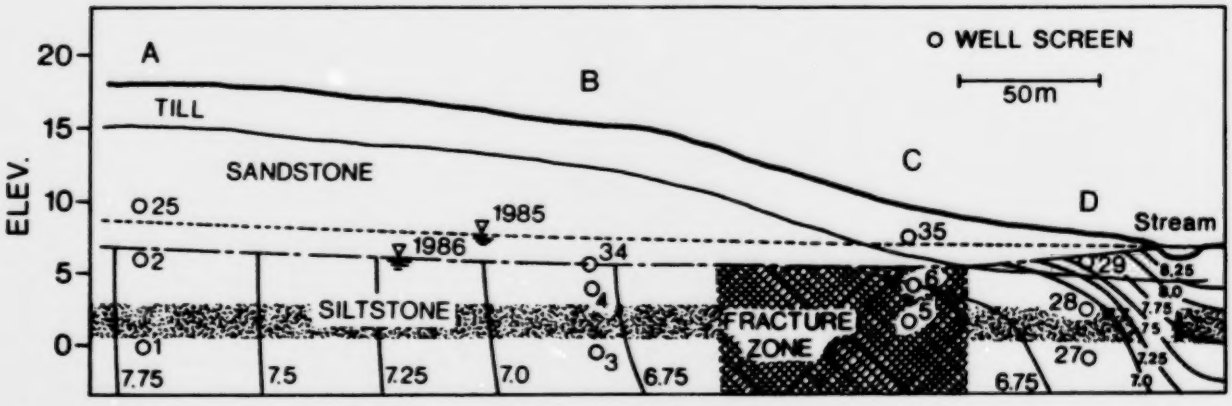


Figure 3b. Piezometric contours in metres above mean sea level, Augustine Cove, P.E.I., September 1986.

pass and during which it is subject to neutralization reactions with authigenic carbonate minerals. A complicating reaction which can cause a pronounced pH decrease would be the oxidation of the NH_4 ion from the applied ammonium nitrate fertilizer:

$$O_2 + (1/2)\,NH_4^+ = (1/2)NO_3 + H^+ + (1/2)H_2O$$

In consuming 8 mg O_2/L, this reaction will produce 0.25 mM H^+ (aqueous pH = 3.6), which will tend to be neutralized by carbonate and oxide minerals in the sandstone. Therefore, it is possible that, in the low temperature (8°C) and low pH environment of the sandstone aquifer, the hydrolytic degradation of the sulfoxide and sulfone species to nontoxic transformation products is being retarded by oxidation reactions such as the one above.

A further complication is posed by the apparent seepage of stream water into the flow system. This surface water, which can be identified by its low aldicarb and nitrate levels, is represented by wells 27 and 5.

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Hydrogeology of the Niagara Frontier

K.S. Novakowski, Study Leader

P.A. Lapcevic

K.S. Novakowski

INTRODUCTION

Over the last decade about 160 hazardous-waste sites have been found to lie within 4.8 km of the Niagara River in New York State. Each of these has the potential to contaminate the groundwater in the shallow subsurface, and a few such as the Hyde Park Landfill and S-Area, have the potential to contaminate deeper groundwater in the fractured Paleozoic sediments which underlie the Niagara frontier. Therefore, because some of this contamination may eventually reach Canadian territory, either by discharge into the Niagara River or by contamination of Canadian groundwaters, it is important for us to better understand the pattern of regional groundwater flow which controls the direction and rate of contaminant migration. The objective of this study is to develop a mathematical or conceptual model of groundwater flow in the Niagara Falls area from detailed information on the hydraulic and chemical transport properties of the fractured bedrock. To fulfill this goal, new hydraulic testing techniques for determining the vertical and horizontal permeability of very low permeability rock will also be developed.

RESEARCH RESULTS

Seven moderately deep N-sized boreholes have been drilled and instrumented with multiple-packer casing strings in the Niagara Falls area over the previous three years. The boreholes are spread over a distance of about 10 km and mostly lie adjacent to the Niagara River. The boreholes were drilled to depths of about 50 m, well into the Queenston Shale Formation, which is currently believed to be the bottom of the regional groundwater flow system.

Detailed hydraulic tests, using long-term shut-in and new stepped-volume slug tests, showed that a broad distribution of hydraulic conductivities between 10^{-5} m/s and 10^{-14} m/s is characteristic of these Paleozoic sediments. Most of the permeability is through bedding-plane fractures and not in the rock matrix or vertical fractures. The most permeable features are found near the top of the bedrock in a weathered-zone and along major time lines such as the Silurian-Ordovician boundary at about 120 m depth.

Hydraulic head measurements were obtained periodically after each hole was drilled. The three-dimensional hydraulic-head distribution shows relative uniformity in the near surface measurements, with very high (up to 40 m above ground surface) hydraulic heads evident in the Rochester shale and Clinton-Cataract groups. The high hydraulic heads are a result of the presence of natural gas at various horizons in the Lower Silurian rock. The Silurian-Ordovician boundary shows very low hydraulic heads (as much as 60 m below ground surface), which indicate a strong lateral hydraulic connection to the Niagara Gorge below Niagara Falls.

Inorganic and stable isotope geochemistries obtained from groundwater samples suggest very old water in the zones associated with natural gas and young water near the top of the bedrock and at the Silurian-Ordovician boundary. Stable isotope chemistry in the near-surface samples show good vertical hydraulic communication between the bedrock and the Upper Niagara River. Organic chemistry indicates that the Rochester Shale Formation is currently producing natural hydrocarbons at levels high enough to interfere with contaminant detection.

Predicting the Migration of Dense Non-Aqueous Phase Liquids in Fractured Rock

K.S. Novakowski, Study Leader

P.A. Lapcevic

INTRODUCTION

A significant proportion (perhaps 30%-40%) of the hazardous-waste sites which lie adjacent to the Niagara River in New York State (and many elsewhere in North America) are underlain by fractured bedrock which is in direct hydraulic communication with the overlying contaminated material. Most of these sites have some proportion of dense non-aqueous phase liquid (DNAPL) contaminants, small or large as in the case for Hyde Park Landfill, which have seeped into the fractured rock and migrated along vertical fractures and bedding plane partings. Because DNAPL migrates under gravity potential and capillary, it is very difficult to predict, with our current knowledge, the direction and rate of DNAPL movement, particularly in geologically complex bedrock material. The objective of this study is to define more quantitatively the parameters that must influence DNAPL migration and to provide conceptual and mathematical models with which more accurate site assessment and more effective remedial action can be undertaken.

RESEARCH RESULTS

A review of literature pertaining to the migration of DNAPL in geological materials is nearing completion. The results show that despite the large body of petroleum literature, there are virtually no hard numbers available for parameters such as relative permeability that have been obtained at scales and with materials of interest to a contaminant hydrogeologist. Therefore, this study will begin by focusing on the most basic parameters at small scale in a well-controlled laboratory environment.

The intent of our laboratory program is to simulate natural single rock fractures in the lab and on computer so that we may simulate DNAPL transport in our models at the appropriate scales. Currently, we are designing a casting procedure in which samples of natural rock fractures at about 1-m scale will be copied by casting using resins and grout on each fracture face. The cast pair will be mated and hydraulic experiments conducted in each model. The design of the casting procedure is complete and space for the experiments has been obtained in the hydraulics laboratory.

The natural fracture samples will also be simulated using a computer. One way this can be done is by obtaining a representative aperture distribution from the samples, using either a machinist's profilometer or photographic techniques and regenerating the distribution randomly or with auto-correlation in a spatial grid on computer. The various non-linear equations describing flow and transport can then be solved within the grid. Software for generating the aperture distribution and solving for aqueous phase velocity using finite-difference methods has been written and will soon be tested.

Another technique for simulating fracture surfaces is by using fractal geometry. Aperture distributions can often be described by a single number, the fractal dimension, and easily reproduced with simple algorithms based on fractal theory. The resultant representation of a fracture surface can be very similar but not necessarily identical to that from which the fractal dimension was obtained. A FORTRAN program which generates fractal polygons from a fractal dimension has been obtained from Alain Fornier (Xerox Park, Calif.) and will be adapted to generate fracture surfaces onto a finite-difference/finite-element grid. Again the various flow and transport equations can then be solved.

Sample collection began in the spring of 1987 and experimentation with cast reproduction is planned to begin in the winter of 1987/88. Software development will be ongoing.

Water Quantity Modelling/Monitoring

Y.L. Lau, Project Chief

Y.L. Lau

ISSUE AND RATIONALE

Rivers provide water for human consumption, agricultural and industrial needs, hydropower, recreation and many other uses. They can also cause loss of human life and severe damage to property through floods, droughts and erosion. Rivers are also the receiving grounds for industrial and municipal waste discharges as well as contaminants from many diffuse sources. With all these conflicting uses and demands it is necessary to understand the dynamics of river flow and the interaction of rivers with all their boundaries in order to provide wise management of water resources and to devise solutions to environmental problems.

Sound management decisions require the ability to predict the effects of any changes affecting water resources. The only practical way of making these predictions is by the use of mathematical models. However, mathematical models must be based on firm scientific knowledge,and they are only as reliable as the equations and relationships which they employ. Therefore, the development of predictive models has to go hand-in-hand with basic processes research.

The fate of the contaminants which a river receives depends on transport and mixing processes and the interaction between the water, the sediments, and ecological processes. Of particular importance is the role played by fine-grained sediments in the transport process. The fine sediments may carry a significant amount of pollutants in particulate form. In addition, the sorption process can directly or indirectly affect the pollutant degradation by altering the solution phase concentration and affecting the solution phase reaction. Sediments on the river bottom can act as sources or sinks of contaminants. Research is needed to develop new knowledge on the processes of flocculation and settling and on the tractive forces required for the movement and resuspension of sediments from the river bottom so that these processes can be properly incorporated into models of contaminant transport.

Nonpoint sources of pollution can have significant effects on the water quality. In order to delineate these effects one must have the capability of modelling the processes involved in the transport of nonpoint source pollutants including the hydrological response of the watershed, the sediment loss during runoff-events and the interaction of various pollutants with sediment loss and runoff.

Although nonpoint sources contribute to pollution only during runoff producing events, processes between these events can determine the runoff quantity and quality. Therefore one must be able to simulate the hydrological and water quality related processes in the watershed on a continuous basis. Because water resource or land use developments can significantly alter the hydrological response of a watershed, it is necessary to be able to model the effect of such developments on the precipitation-runoff relationship. The collection of data for the calibration and assessment of watershed models is an essential activity for this purpose.

Much work has been done towards simulating the general response of urban watersheds to various development or management alternatives. Such work will be further advanced by focusing in detail on the underlying water quantity and quality processes. This expertise will be further developed and modified for use in rural watersheds and river basins. Soil-water interactions under various land use practices are of particular interest. Emerging water resource issues deserving further attention include the effects of agricultural practices on water resources and migration of agricultural chemicals.

While the interaction between fine sediments and river flow is important for the transport of contaminants, the movement of coarse sediments plays an important role in determining the flow regime, river level, etc. Besides causing problems such as flooding and sedimentation, changes in river regime can lead to changes in vegetation, wildlife and water quality. Research is required into the processes of coarse sediment transport and the interaction between

the flow and the banks so that models can be developed to predict changes in river regime which may be caused by any proposed developments such as interbasin diversions.

Flooding is a problem which occurs in many rivers and is very difficult to predict and control, especially when compounded by the presence of ice jams. The predicting of the location and severity of ice jams, the flood levels caused by jamming, and methods of controlling ice jams all require new knowledge on the mechanics of ice jams and the interaction between the stable ice cover and ice floes. The production of frazil ice and anchor ice changes the flow resistance and water levels and makes river flow measurement in winter unreliable. All river developments affect the ice regime and knowledge and expertise on river ice are required to answer questions dealing the often conflicting demands on power generation, navigation and northern development. Ice jam research is a relatively new field and much still has to be learned before reliable predictions can be made.

LONG-TERM OBJECTIVES

To develop knowledge and expertise on the processes and the implications of open-water and ice-covered river flows, the transport of fine and coarse grained sediments and on the movements of contaminants through the land water interface so as to provide guidance in formulating management strategies and departmental responses on water resources issues in the nation's rivers.

River Flow and Sediment Transport

Y.L. Lau, Study Leader

B.G. Krishnappan, V. Chu (McGill University) and
G. Luk (Queen's University)

INTRODUCTION

Rivers provide water for many varied and conflicting uses. In order to manage river resources wisely and to predict or solve environmental problems, one must understand the dynamics of river flows and be able to model the movement of the water and the sediments. To do so requires research into the basic flow and sediment transport processes and the development of predictive models.

The shear stresses which the flow imposes on the river bottom creates bed forms which in turn changes the flow resistance, the water level and flow velocity. Knowledge on the relationship between bed form and flow resistance is still incomplete. In tidal rivers the situation is even more complicated because of flow reversals.

The diffusion in suspension is known to affect the velocity and resistance of channel flows. It stands to reason that the diffusion characteristics of the flow should also be altered when suspended sediments are present. This effect still needs to be investigated.

Meanders alter the flow pattern and flow resistance. Knowledge of meandering flows still needs to be developed in order to facilitate the development of a two dimensional river model.

RESEARCH RESULTS

Based on laboratory investigations using artificial bed forms, it was found that the flow resistance caused by ripples is actually decreased when the flow reverses in direction. Calculations then revealed that this reverse flow situation occurs in the Pitt River which is a tributary of the Fraser River in British Columbia. This result is useful for the modelling of the Lower Fraser by the Inland Waters/Lands Directorate (IW/LD).

The effect of suspended sediments on mixing in open channel flows was investigated in a series of flume experiments. It was found that the presence of sediments reduces turbulent diffusion, mainly through the reduction of the length scale of the turbulence, while the intensity of turbulence was relatively unaffected.

A two-dimensional model of river mixing, capable of simulating unsteady input of pollutants, was developed. This model can account for real river features such as variations in depth and velocity as well as river curvature. Preparations have been made for laboratory verification of the model.

Measurements of bed load and suspended load sediment transport were made at several transects in the St. Clair and Detroit rivers. This information is being used with measurements of pollutant concentrations in the water as well as in the sediments to determine the manner in which the total pollutant load is being distributed.

Work continued on a task group formed under the Canadian Society for Civil Engineering to evaluate various river flow models available in the literature. A report comparing the theoretical formulations and the strengths and weaknesses of the models has been written.

An apparatus to investigate meandering flows with or without ice covers was designed and fabricated. Experiments will begin shortly.

Various technology transfer work was carried out, including presenting three workshops to instruct IW/LD personnel on the use of the RIVMIX and MOBED models, working for the IJC committee on the Flathead River, organizing the IAHR symposium on scale effects in modelling sediment transport in Toronto, and planning for a symposium on interbasin transfer of water.

PUBLICATIONS

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Ice Jams and Floods

S. Beltaos, Study Leader

J. Wong

S. Beltaos

INTRODUCTION

Canadian rivers are subject to major flooding caused by ice jams. Tangible annual damages in Canada exceed $35 million, while intangible damages are very serious, including loss of life. The cost of ice-jam damages is likely to increase in the future, owing to increasing urbanization.

Decision-makers need sound river ice management methods and data in order to evaluate long-term flood risk and damage, to select suitable control measures, to design and implement effective short-term responses to threatening ice jams, and to assess the environmental impact of resource development. However, scientific knowledge on ice jams is presently in an infantile stage, owing to the extreme complexity of the attendant natural processes as well as to the limited research effort expended to date.

New knowledge must be developed regarding conditions of formation and release of ice jams, formation and breakup of the river ice cover and computer models simulating the ice regime of rivers. Starting in 1979, these needs have been addressed at NWRI via systematic observation of the ice regime at selected river reaches; laboratory experimentation on specific ice jam phenomena amenable to study under controlled conditions; and theoretical analysis and development of mathematical models.

RESEARCH RESULTS

Analysis of previous years' field observations on the Grand and Thames rivers has provided further support for NWRI-developed methods to forecast the onset of river ice breakup and the flooding potential of ice jams.

Work continued on development of a material that will adequately model the laboratory experiments at room temperature. Tests of the interaction between jams and model "ice" sheets have shown very good performance of the material. It is planned to investigate the possibility of obtaining patent rights for the model "ice."

A numerical model, developed earlier to predict the configuration of ice jams in prismatic channels, has been suitably modified for applications to natural streams.

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Sediment and Water Flow

B.G. Krishnappan, Study Leader

P. Engel, D. Doede and F. Dunnett

B.G. Krishnappan

INTRODUCTION

Mathematical modelling of river flows requires basic knowledge in a number of aspects of sediment-water interactions. For example, the formation of dunes and ripples on the river bed and the formation of meanders affect the resistance characteristics of river flow which in turn influence its sediment-transporting capacity. The effect of dunes on the friction factor of the mobile boundary flows and the formation of meanders were investigated in laboratory channels under this study.

RESEARCH RESULTS

The experimental data on the effect of dunes on friction factor of mobile boundary flows have provided quantitative information on scale effects of physical models of sediment transport. The experiments on meander formation have shed new light on factors influencing the formation of meanders.

PUBLICATIONS

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Mathematical Modelling of St. Marys River

B.G. Krishnappan, Study Leader

P. Yee, S. Moin and W. Bien

INTRODUCTION

Dredging of the St. Marys River west of Sugar Island on the American side has been suspected in producing changes in the flow distribution around the island. Reduced flow on the Canadian side has produced water quality degradation and shoreline changes in the Lake George channel. A mathematical model to predict the effect of dredging in the St. Marys River system is required to pinpoint the actual cause.

RESEARCH RESULTS

A modelling strategy has been developed to model flows and sediment deposition in the St. Marys River system. This involves integration of two existing river models: MOBED and FERNS. Actual flow simulation using data from St. Marys River will be carried out during the current study year.

PUBLICATIONS

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Urban Water Resources

J. Marsalek, Study Leader

H. Ng, J. Heidt and R. Stephens

J. Marsalek

INTRODUCTION

An ever-increasing proportion of the Canadian population lives in urban areas. Recent surveys indicate that the Canadian urban population represents more than 80% of the total population and such a percentage is even higher in the most populous provinces. High concentration of urban populations in relatively small areas creates conflicting demands and stresses on water resources. The demands include water supply, waste disposal, flood protection and water-based recreation. The conflicting stresses caused by urban population include increased pollution of surface waters and groundwater, and increased surface runoff and incidence of flooding. The goal of urban water resources studies is to provide solutions to water resource problems by satisfying the demands and minimizing the environmental stresses.

The activities conducted under this study in 1986/87 included investigations of the effects of river basin urbanization on streamflow, effects of urban land use on runoff quality, effects of runoff on water quality in Hamilton Harbour, editorial work on two UNESCO drainage manuals, and investigations of flow measurement structures for clients.

RESEARCH RESULTS

Progressing urbanization of the Waterford River Basin is adversely affecting water resources in the basin. There are concerns that further land development in the basin will lead to further deterioration of the state of water resources in the basin, unless proper control measures are adopted. To assess such impacts, it was desirable to simulate streamflow in the Waterford River and the changes resulting from future land use changes. Such a task has been accomplished by means of a continuous simulation model which, after calibration, reproduced well both low and high flows in the river. In a future land use scenario assuming the doubling of the impervious surfaces in the basin, the annual streamflow volume would be hardly affected, but the highest peak flows would increase by as much as 20%. Such increases are significant and would increase the flooding of low laying areas of the basin.

The effects of urban land use on runoff quantity have been investigated for commercial and light industrial land use. Runoff composition has been characterized for conventional pollutants in terms of mean concentrations, annual unit loadings, and frequency distributions of pollutant concentrations. The results indicate that in well-maintained urban areas, the overall runoff quality is barely affected by the land use and both commercial and light industrial areas may produce runoff quality comparable to that in clean residential areas. Such findings contradict the general assumptions frequently made in runoff modelling approaches.

Urban runoff has been investigated as a source of toxic contaminants in the Upper Great Lakes Connecting Channels Area. Using the results of field sampling of runoff quality and computer simulations of runoff flows, preliminary estimates of annual loadings of selected substances in runoff have been produced and supplied to the modelling group for this project. Further refinement of such estimates is under way, as more analytical data is returning from the water quality laboratory. A final report is due this fiscal year.

In preparation for future contributions to the Hamilton Harbour Study, a review of the effects of surface runoff on water quality in the harbor has been completed. Two types of such effects are distinguished: the loadings of various materials carried by runoff and the effects of runoff inflow on transport processes in the harbor. A proposal for further contributions in the form of a loading model has been made.

Under the UNESCO International Hydrological Programme (IHP), editorial work on two manuals on urban drainage has been completed. These manuals deal with technical aspects of drainage design and the collection of supporting data. Recognizing the strong coupling between

drainage and water quality in receiving waters, these manuals should be particularly useful in urban water resources management in developing countries. Both manuals will be submitted by UNESCO for printing shortly.

Effective operation of wastewater treatment plants and fair allocation of operating costs require accurate flow measurements in sewage collection and treatment systems. Following the identification of serious measurement problems at the Richmond Hill III Flow Measurement Facility, the Ministry of the Environment has commissioned NWRI to evaluate this facility and to propose remedial measures. Structural changes of the facility have been proposed to the Ministry and subsequently implemented. The accuracy of flow measurements at the facility has been significantly improved.

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Ecotoxicology

B.J. Dutka, Project Chief

B.J. Dutka

Biological monitoring methods in water quality studies are used for two main reasons: to determine ecological effects and to determine possible contamination in the environment (either natural or anthropogenic). The strength of biomonitoring techniques lies primarily in the close simulation of biomonitors with the systems under study. Thus, aquatic organisms provide monitoring capabilities which take into account the actual responses of organisms or populations to environmental variables including other pollutants with which interactions may occur. In contrast, chemical measurements, however precise, still have to be interpreted in context of a complex set of factors operating within ecosystems. Interpretations of precise chemical measurements obtained from laboratory dose-response experiments are unlikely to be wholly reliable guides to what happens under field conditions. Indeed, the degree of effect of the pollutant may vary according to the presence or absence of other stresses on the biological system and this may produce interaction effects which could be antagonistic, additive or synergistic. Furthermore, the collection and retention properties of biological monitors, eg., for airborne particulate pollutants, will be much more representative of the field conditions than physical monitoring devices such as deposit gauges or high volume air samplers.

PROJECT OBJECTIVES

The objectives of the project are to develop new and improved biomonitoring techniques for the assessment of water quality and the health of aquatic ecosystems.

For *in situ* studies, biological species will be selected based on the following criteria: their ability to bioaccumulate (qualitatively and quantitatively); their availability (geographically and seasonally); their specificity of uptake; their repeatability or reliability; and cost of collection and analysis.

Many enzyme, bacterial and algal tests have been developed for the monitoring or screening of toxicant/genotoxicant/mutagenic effects in effluents, waters and sediments. The majority of these tests are rapid, simple, relatively reproducible and inexpensive, and require little space and time as compared to fish and cladoceran tests. However, little information is available on comparative studies of short-term microbial assays for estimating the impact of toxicants on the aquatic environment. Such studies could give valuable information on reproducibility, sensitivity, cost and rapidity of the various tests.

Also due to escalating costs and transportation problems, traditional and newer proposed microbiological tests for water and sediments must be reevaluated. In this reevaluation process, bias should be given to those tests which are amenable to short-term refrigeration/preservation (48-96 hr), are easy to perform and do not require excessively sophisticated equipment and specialized staff, and are cost effective.

In our studies we will evaluate the suitability of a variety of microbiological, biochemical and toxicant screening tests to become part of a battery of tests. The final goal of these evaluation studies will be to develop a battery of tests containing two or three toxicant/genotoxicant screening tests and two or three microbiological hazard screening tests which can be used nationally or internationally to designate and priorize specific water bodies and sediments that are degraded or are being degraded for further investigation or remedial action.

Microbial Toxicity Screening Methods, Evaluation and Testing

B.J. Dutka, Study Leader

K. Jones and Hao Xu (Visiting Scholar from the People's Republic of China)

INTRODUCTION

With increased world-wide industrialization over the past 25 years, and with the concomitant higher demand for chemicals, Canadians face increasing ecological and toxicological problems from the release of toxic contaminants to the environment. In response to these expanding stresses on the environment and in the belief that there is no single criterion by which to adequately judge the potential hazard (either to the environment or man) of a given substance, a multitude of biological assay procedures have been developed, proposed and used to assess toxicant impacts. Due to our newly acquired awareness of the long-term effects of chemicals discharged into receiving waters, research efforts are being directed at short-term bioassay tests in an attempt to alert monitoring agencies as well as dischargers of toxic conditions. Since the Water Quality Branch (WQB) monitoring program of the Inland Waters/Lands Directorate is becoming more involved with biological and bioassay parameters, one of the goals of this study is to assist WQB personnel in making appropriate selections of tests by evaluating various toxicity screening procedures. Specifically, the prime goal of this study was to evaluate the ATP-TOX System and SOS Chromotest kit as potential members of a battery of toxicant screening tests.

RESEARCH RESULTS

The ATP-TOX System and SOS Chromotest were applied to water and sediment samples collected from Lake Erie, the Detroit River, the Niagara River and from Saint John River basin waters. The ATP-TOX System has proven to be a very sensitive toxicant screening test, often showing a positive toxicant response when there was none shown by the Microtox test.

The SOS Chromotest has proven to be a valuable test for genotoxic effects. There appears, however, to be a problem with batch-to-batch variation in the testing organism. The samples tested during November and December 1986 and January 1987 all were tested with SOS kits that produced only 25% to 50% of the response of earlier kits, as assessed by positive control responses.

PUBLICATIONS

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Bacterial Toxicity Screening and Water Quality Symposia

B.J. Dutka, Study Leader

D. Liu

INTRODUCTION

The Boundary Waters Treaty (1909) and the Canada Water Act (1970) provide the legislative base for federal involvement in water issues and activities. The Inland Waters/Lands Directorate (IW/LD) of Environment Canada is the agency charged with carrying out the federal government's water management responsibilities, through its various research and monitoring arms.

The resolution of many water issues requires direct research responses. The majority of Canada's water quality research is carried out at the National Water Research Institute (NWRI), which has over the past 15 years become recognized as a world-leading water quality research institute.

As water pollution is a global problem, this problem requires input from scientists all over the world. International symposia featuring or initiated by NWRI scientists have proven to be ideal vehicles for enhancing our knowledge behavior and techniques in the management of our waters—Canada's most valuable resource.

Knowledge is a powerful tool which can be directed towards good applied research that can satisfy immediate needs. Through symposia, conferences or workshops sponsored or initiated by NWRI, international knowledge is synthesized through NWRI scientists for the benefit of Canadian water quality management.

RESEARCH RESULTS

Two international symposia have been initiated through this project. The first was the Third International Symposium on Toxicity Testing Using Microbial Systems, May 11-15, 1987, in Valencia, Spain. This symposium is sponsored by three private international companies and organized by Rivers Research Branch scientists. The primary aim of this series of symposia is to provide a biennial forum for researchers and users to evaluate and discuss toxicity assessment using microorganisms. These symposia are also intended to stimulate communication and cooperation between international researchers and users through the presentation of reports on the development and application of microbial technology in toxicity assessment. For the Valencia symposium, 59 papers were received, representing 21 different countries.

The second symposium is the First Biennial Water Quality Symposium: Microbiological Aspects, August 29-September 2, 1988, Banff Centre, Banff, Alberta. This symposium is co-sponsored by WHO, PAHO, IORC, Environment Canada, Health and Welfare Canada, and Alberta Environment. This symposium series was initiated to respond to the need for a specialized forum dealing with microbiological contamination and hazards in water, and methods to assess and remove these hazards and contaminants. The objective of this meeting is to bring an international view to global water quality problems and to discuss the "hows and whys" of water quality criteria, objectives and standards. Thirteen specialized session /workshops have been consolidated for this symposium representing 55 papers. A total of 110-120 papers are expected to be presented at this symposium.

Water Quality Methods Development Biological Project 86-625

B.J. Dutka, Study Leader

INTRODUCTION

The microbiology laboratories in NWRI have had a methods manual entitled "Methods for Microbiological Analysis of Waters, Wastewaters and Sediments" edited by B.J. Dutka, which detailed in cookbook style all the methods used by microbiology personnel for analysis of water, wastewaters and sediments. Each technique described in this manual had been field-tested and found to be reliable. Since the issue of this manual in 1978, approximately 1000 copies have been sent (at the receiver's request) to almost every country in the world that performed microbiological analysis of water.

However, since the manual was produced in 1978, many new techniques have been evaluated, some have been developed and some of the older techniques have been updated.

Thus, in 1986, a start was made to update this manual by including techniques on toxicant screening, coliphage enumeration, and *Legionella organism* enumeration and adding a section on quality control.

Once the update has been completed (1988), the manual will be translated into French and both English and French editions will be published.

The title of this new revised manual will be Methods Manual for Microbiological and Toxicological Analysis of Water, Wastewater and Sediments.

Microbiological and Toxicity Screening Support to IW/LD and NWRI Studies

K.K. Kwan, Study Leader

B.J. Dutka and K. Jones

K.K. Kwan

INTRODUCTION

This study was carried out to obtain baseline information on toxicant level and distribution in the Bruce Bay near Bruce Mines, North Channel Lake Huron.

The Saint John River basin and Lake Erie areas were chosen for the study since they have industrial chemicals, pulp and paper mill effluents, metal and food by-product contaminants as well as pollution from domestic and farm wastes. These studies were performed using the multiple parameter application technique (toxicity and/or microbiology) to ascertain the nature and effect of toxicity in the study sites, to identify areas of concern and to obtain a data base.

Chemical analysis of sediments, even though providing useful information on the toxicant composition of sediments, does not provide information on the degree of toxicity. The toxic effect of a sediment can only be measured by biological means. Many of the preferred biological tests being used are based on microbial or microbial enzyme activity. Therefore, the use of solvents other than water may influence the outcome of a microbiological toxicity screening test. The study has been initiated to evaluate Mill-Q-reagent grade water (low response water) and lake water (1 m from the bottom) as potential solvents to extract sediment samples collected from Lac St-Louis.

RESEARCH RESULTS

Twelve sediment cores and six water samples were collected from three sampling sites in Bruce Bay near Bruce Mines during May and July 1986. In May sediment samples, toxicants were detected via the Microtox toxicity test in layers 12-14 cm, 14-16 cm, 16-18 cm and 18-20 cm of station 1 cores. Weak toxicity (0.49 gm) was also detected in 6-7 cm layer of the May cores collected at station 3. No toxicants were detected from 1X and 10X water samples via *Spirillum volutans* tests. Data indicate that only low levels of toxicity were found in the sediment and this toxic activity occurred only in the deeper sediments. These findings suggest that a decrease on cessation of discharge of water soluble toxicants had occurred several years ago.

Forty sediments and water samples were collected from the Lake Erie area during the month of June 1986. Thirty-eight sediment and water samples were also collected from the Saint John River basin area during the month of October 1986. All sediment and water samples were subjected to microbial toxicity and microbiological bioassay tests. Results were used to characterize the study sites and to identify the areas of concern. Data indicate that the multiple bioassay test approach is useful and can provide more realistic evaluation of the toxicity and microbial activities in water and sediments.

PUBLICATIONS

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Kwan, K.K. and Dutka, B.J. Report on toxicity screening test studies on water and sediment samples collected from Bruce Bay near Bruce Mines, North Channel Lake Huron. Report 140-AMD-5-86.

Kwan, K.K. and Dutka, B.J. Comparison of sediment toxicant extraction procedure for Microtox toxicity screening tests. Report 139-AMD-5-86.

Great Lakes Surveillance — Interpretation

S.S. Rao, Study Leader

A.A. Jurkovic and J.P. Sherry

S.S. Rao

INTRODUCTION

This project is responsible for the collection, analysis and interpretation of the vast quantity of microbiological data generated during the Lake Ontario Surveillance Program. As part of the International Joint Commission (IJC) Surveillance Program, the Ecotoxicology Laboratory staff participated in the four lakewide cruises (spring through winter) processing over 800 epilimnetic water samples for the lake microbial densities and community structure to define temporal and spatial distributions of microbial biomass in Lake Ontario. In addition, nearly 200 surface water samples were collected and processed for aquatic yeast/fungal populations in order to assess the potential usefulness of aquatic fungi as indicators of water pollution in a large lake.

RESEARCH RESULTS

As the heterotrophic bacterial populations are directly affected by nutrient levels, these populations should reflect conditions of nutrient input and control measures. Similarly, total and actively respiring bacterial measurements are vital for understanding energy flow in aquatic ecosystems. In general, bacterial distribution patterns clearly identify point sources where introduction of degraded water is suspected as well as delineate areas influenced by these point source inputs. From the summarized data, heterotrophic bacterial populations indicate the potential areas of concern: Niagara River mouth, areas near Metropolitan Toronto, Oswego and the Black Bay River area.

Based on the bacterial biomass distribution pattern, it is suspected that Lake Ontario may not be experiencing an overall significant increase of limiting nutrients, thus allowing the bacterial populations to maintain existing levels over the years. The information on bacterial biomass and respiring bacterial densities, along with the information on productivity measurements on Lake Ontario phytoplankton, will be used to establish seasonal energy flow through bacteria to other components of the lake ecosystem.

Preliminary analysis of the data on the distribution pattern of aquatic fungal populations indicate that fungal populations have potential value for detecting problem areas or areas of concern in the large lake.

Effects of Acidification on Organic Matter Biodegradation in Lake Sediments

S.S. Rao, Study Leader

A.A. Jurkovic and B.K. Burnison

INTRODUCTION

This project aims to gather information on microbiological/biogeochemical processes in lakes receiving acidic deposition in order to understand the impact of Long Range Transport of Airborne Pollutants (LRTAP) on Canadian surface waters. LRTAP is well recognized as a high priority research issue both by the scientific community and by all levels of government. As part of the LRTAP overall program, Ecotoxicology Laboratory personnel (Rivers Research Branch) in collaboration with Nutrient/Contaminant Interactions group (Lakes Research Branch) studied microbial biodegradation of organic matter in acidified lake sediments. Organic matter biodegradation studies were conducted using manometric respirometry and mineralization of ^{14}C-labelled compounds. All measurements were normalized to the same temperatures.

RESEARCH RESULTS

The microbial oxygen consumption rate and bacterial numbers were greater in the non-acid stressed lake sediments. The oxygen consumption rates in the acid lake sediments were approximately 20 times longer and bacterial numbers approximately 15 times greater than the non-acid lake. However, the uptake and respiration of organics, ^{14}C glucose and ^{14}C glutamic acid by bacteria in acidified lake sediments did not correspond to the values determined by manometric respiration. It was established that the ^{14}C-labelled compounds are not always suitable for measuring the effects of lake acidification due to potential adsorption of ^{14}C substrate to sediments..

Another aspect of the lake acidification process studied was the accumulation of sulfur in the surface sediments. This study provided information on the role of sulfur cycle bacteria in the anoxic subsurface zone to lake sediments. Results clearly indicated that sulfate-reducing bacteria in the subsurface layers of the lake sediments contributed to the exessive surface sulfur accumulation by bacterial sulfate reduction.

PUBLICATIONS

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Nriagu, J.O. and Rao, S.S. 1986. Response of lake sediments to changes in all metal emissions from smelters at Sudbury, Ontario. NWRI Contribution 86-84.

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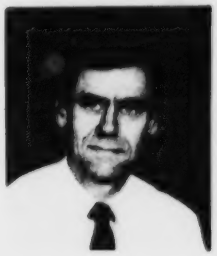
Research and Applications Branch

John Lawrence, Director



John Lawrence

The Research and Applications Branch of the National Water Research Institute conducts mission-oriented basic and applied research in areas of analytical chemistry and hydraulics. It is also responsible for transferring research and technology to the operational sectors of the Department of Environment and for providing technical and scientific services such as current meter calibration, sedimentology and geotechnical services and analytical quality assurance. The work addresses priority issues of the Inland Waters/Lands Directorate and other agencies of the Department.

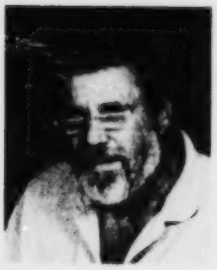
New, improved and more cost effective analytical techniques (including laboratory automation) are developed and evaluated for the measurement of priority chemical and biochemical parameters in environmental matrices. The Branch also has lead responsibility for analytical quality assurance for most Conservation and Protection (C&P) chemical monitoring programs. The major clients for this analytical work include the National Water Research Institute, the Water Quality Branch national and regional laboratories, federal-provincial water quality agreements, the program on Long Range Transport of Airborne Pollutants, the Prairie Provinces Water Board and the Great Lakes Water Quality Program.

New knowledge of the dynamics of water is sought to provide a framework for the management of water resources, and for biology and chemistry research in the aquatic environment. The interfaces between water and the atmosphere, bottom sediments, and shore are studied to explain the mechanisms controlling the transport of pollutants and erosion. Advances are made in river metrology to improve management of that resource. The major clients are the Water Resources Branch, Water Planning and Management Branch, Great Lakes Water Quality Program, Environmental Protection, and the Atmospheric Environment Service.

Universities and private industry are encouraged to make use of the Branch facilities and expertise either by collaborative studies with the professional staff or leasing of the facility with or without technical support. The Branch maintains a well-equipped hydraulics laboratory, sedimentology and geotechnical laboratories and a special clean and hazardous chemicals laboratory in addition to conventional chemical laboratories. The cost of all direct requests from external agencies are cost recovered, in full or in part, in accordance with the Treasury Board Cost Recovery Policy.

Analytical Chemistry Research

I. Sekerka, Project Chief



I. Sekerka

SYNOPSIS

The mandate of the project is to advance knowledge and provide expertise on environmental analytical chemistry. The project is essential for the successful management and utilization of water resources and for research on water pollution, especially the identification of emerging problems.

ISSUES AND RATIONALE

Successful solutions to environmental problems require the availability of accurate, precise and rapidly produced analytical data. Every department program which relies on the collection of data is dependent on the availability of sound chemical methodology.

This project develops and evaluated analytical methodologies (including sample collection, preservation, extraction, pre-concentration, cleanup and analysis) for the measurement of chemical parameters in water, sediment, effluents and biota. Improvements to existing methods in terms of precision, accuracy, detection limits, cost effectiveness, automation and speciation are an integral part of the program.

Project activities include advanced analytical chemistry research as well as methodology support and transfer to IW/LD laboratories, NWRI scientists, the GLWQP and other clients.

PROJECT OBJECTIVES

1. To develop new and improved analytical methods as well as screening and sampling procedures which are accurate, cost-effective, sensitive and unambiguous for the identification and quantification of contaminants in aquatic ecosystems.
2. To play the lead role in documentation, validation and standardization of analytical methodologies to ensure accuracy and reliability of analytical data.
3. To provide the services of sophisticated instrumentation and facilities such as gas chromatography-mass spectrometry and the Clean and Hazardous Chemicals Laboratory.
4. To transfer developed methods and technologies to the national and regional laboratories of IW/LD and to other clients.

RESEARCH PROGRAM

Analytical methods will be developed for organic and inorganic parameters in a variety of environmental substrates. These include state-of-the art techniques such as high performance gas chromatography, high pressure liquid chromatography, emission and absorption spectroscopy, flow-injection analysis, radioimmunoassay and electrochemical techniques. Both broad screening techniques and detailed quantitative techniques will be developed, as well as improved sample collection and extraction techniques.

CURRENT ACTIVITIES

1. Analytical/Methodological

- Implement dense-gas (supercritical fluid) chromatography in tandem with low resolution mass spectrometry for analyzing priority organic contaminants.
- Develop electrochemical and flow-injection analytical methods to improve economy and efficiency of operations in WQB laboratories.

- Develop screening methods for interference in sediment and large volume water concentrates prior to GC and capillary GC analysis.

- Develop cleanup procedures suitable for analysis of dioxins, furans and sulphur-containing compounds.

- Develop a method for simultaneous determination of 5 anions and up to 5 cations by ion chromatography.

2. Laboratory Service

- Provide the service of the Clean and Hazardous Chemicals Laboratory.

- Automate and computerize laboratory analytical systems for application in the NWQL.

3. Field Samplers

- Develop large-sample extractor for field use.

Electrochemistry and Flow Injection Analysis

I. Sekerka, Study Leader

J.F. Lechner

INTRODUCTION

Electroanalytical techniques have been used for a variety of applications because of their high sensitivity, their response to cations, anions and organic functional groups, and the ability to determine multiple analytes in a single procedure. They are very powerful analytical tools when combined with separation techniques, e.g., GC, IC, HPLC, etc.

Flow injection analysis (FIA) is based on the injection of a liquid sample into a moving carrier stream. The stream mixes with reagent solutions and the resulting reaction products are continuously recorded by a suitable detector. FIA is an automated microchemical technique capable of high sampling rate with minimum sample and reagent consumption.

The research and development of electroanalytical and flow injection methodologies is aimed towards the improvement of the economy and efficiency of the National Water Quality Laboratory (NWQL) and other laboratories and the maintenance of state-of-the-art expertise in modern environmental analytical chemistry .

RESEARCH RESULTS

1. A comparative study of various methods for low levels of cyanide has been concluded. The amperometric FIA method with the gas permeable cell developed in our laboratory has been found to be a superior technique. The only interference caused by S^{2-} compounds has been eliminated by the addition of Bi^{3+}. The achieved lower limit of detection is 0.2 ppb using a 500 µl sample injection at the sampling rate of 60 samples per hour. A report is in preparation and the technology transfer to Western and Northern Region was accomplished in June 1987. Recently it was found that the chemiluminescence reaction between cyanide ion and "organized surfactant assemblies" fortified by fluorescein is sufficiently sensitive for low levels of cyanide determination. Its incorporation into previously developed FIA systems gives the user the choice of two detectors and enhances the flexibility of the stop and go gas permeable flow system.

2. An FIA method for simultaneous FIA-flame photometric determination of Na and K is ready for technology transfer.

3. Automation of the FIA technique has progressed by interfacing ICAP to FIA and by designing bottle-labelling and label reading devices. Also, two variations of the system for bottle introduction, sample identification and transmission were designed. One system uses a robotic arm whereas the second system is based on a conveyor belt principle. The final choice is the robotic system. The required instrumentation (robot and laser label reader) has been purchased and is being tested and modified. Necessary software for the system operation was prepared.

4. The previously developed method for the determination of alkalinity and acidity by conductometric titration has been computerized and interfaced to the NWQL mainframe computer. It is in full time routine operation.

PUBLICATIONS

Sekerka, I. and Lechner, J.F. 1987. Determination of alkalinity by FIA using conductivity detector. In Focus. In press.

Sekerka, I. and Lechner, J.F. 1987. Analysis for dissolved oxygen in natural water, including sample preservation. Int. J. of Environ. Anal. Chem. In press.

Operation of Clean and Hazardous Chemicals Laboratory and Separation of Trace Organics

I. Sekerka, Study Leader

R.J. Wilkinson

INTRODUCTION

These research and development activities focussed on the evolution of an analytical scheme with a greater degree of applicability to a variety of environmental samples with respect to the isolation and quantitation of polychlorinated dibenzo-p-dioxins (PCDDs).

A considerable effort has been devoted to the operation and maintenance of the Clean and Hazardous Chemicals Laboratory.

RESEARCH RESULTS

Provision of Standards to Various Agencies at CCIW

1. Internal labelled 13 C and 37 Cl standards for the quantitative analysis of dioxins in various matrices have been provided on a regular basis to the National Water Quality Laboratory, the Great Lakes Fisheries Research Board and other laboratories within NWRI.

2. Requests for an internal labelled standard for quantitative analysis of furans have been deferred until financial arrangements for the acquisition of standards are completed between the agencies involved. Native, non-analytical standards of the similarly substituted furans (to the dioxins) are being provided in the interim.

3. A complete set of standards (dioxins and furans) has been received by this laboratory from Northrop Laboratories. These standards will be utilized to determine the response factors and ratios between the ions of the spiked labelled standards and the native ions in an effort to provide a more accurate and precise determination of actual quantities of dioxin and furans in complex organic matrices.

Analysis of Sediment Samples

A cleanup and isolation sequence outline for the analysis of dioxins and furans is now available for technology transfer.

1. A final report covering the analysis of four samples from the Vancouver area submitted by the National Water Quality Laboratory has been completed.

2. Results for the analysis of four samples from the Niagara River have been tabulated and forwarded to NWQL.

3. Three samples from Rainy River submitted by the Water Quality Branch have been analyzed and all yielded recoveries ranging from 55% to 89% based on labelled spiked compounds.

Provision of Services and Facilities

1. Twelve fish samples were extracted for the radioimmunoassay (RIA) dioxin screening technique. The extracts were passed through varying steps for cleanup and isolation to determine the extent of cleanup required for successful analysis.

   A landfill sediment sample, submitted by Surveys and Interpretation, Water Quality Branch, Ottawa, could not be analyzed. Our standard cleanup procedure was not successful and further procedural development will be required to deal with this environmental compartment.

PUBLICATIONS

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Onuska, F.I., Wilkinson, R.J. and Terry K. Isomer-specific separation and quantitation of tetrachloro dibenzo-p-dioxins by HRGC and HRGC/MS. J. High Resolut. Chromatogr. Chromatogr. Commun. In press.

Supercritical Fluid Chromatography

F.I. Onuska, Study Leader

K. Terry

F.I. Onuska

INTRODUCTION

The study of supercritical fluid chromatography (SFC) is part of the ongoing development of new analytical techniques for the analysis of trace organic contaminants in a variety of substrates. SFC methods are designed to assist the National Water Quality Laboratory and regional Water Quality laboratories by providing alternative analytical methods where high resolution gas and liquid chromatographic methods are not adequate.

The goals were defined as follows:

1. to interface the previously designed supercritical fluid chromatography system to a quadrupole mass spectrometer;
2. to develop methodology for determining PAHs and herbicides by means of supercritical fluid chromatography;
3. to provide services to clients in analyzing for dioxins.

RESEARCH RESULTS

At the invitation of the Japan Society for the Promotion of Science, F.I. Onuska participated in a scientific exchange program at Kyoto University, Kyoto, Japan. Achievements during the eight weeks included:

1. Hardware adaptations to enable operation of a supercritical fluid chromatograph at Dr. Rokusika's laboratory;
2. The design and adaptation of low dead volume connectors;
3. Characterization of the effect of column internal diameter on separation efficiency with narrow-bore columns;
4. Application of SFC, covering PAHs and PCBs.

With respect to the selectivity toward PAHs and PCBs, 5% phenol, 95% methylpolysiloxane seems to be a suitable stationary phase, but cyanopropyl siloxane was also evaluated. Separation was run on a 10 m x 50 μm fused-silica OTC-coated, bonded and cross-linked column. The mobile phase was carbon dioxide at 90°C. An average linear velocity of 2 cm/s for a 50 μm i.d. capillary provides the best resolution. Results indicate that capillary SFC has a resolving power remarkably similar to HRGC when longer analysis times are allowed. Density programming of carbon dioxide produces an elution order (selectivity) very similar to gas chromatography. However, a 50 μm i.d. WCOT column requires a maximum injection of 200 nL, which must be split in 1:5 ratio to avoid column overloading. This represents a significant drawback because real amounts of a component present in a solute must be at least 20 mg/mL when a flame ionization detector is used.

To improve transport of the solute to the flame a restrictor must be connected at the end of the OTC. A very elegant solution to this requirement is to produce a well-defined conical closure, which is gently abraded by a microdrilling abrasive rotating disc. It slowly removes the silica surface at the end of the capillary column until the conical end opening is reached. Using this technique, it is possible to produce restrictors with i.d. smaller than 1 μm.

Our instrument has been fully automated. Both the pumping system and the injection system are computer-controlled for added precision in the quantitative analyses.

Some preliminary tests were run on a variety of fungicides and pesticides. This area will be investigated further in the near future.

Analyses for dioxins were performed as requested by our clients.

PUBLICATIONS

Onuska, F.I. 1986. Report to the Japan Society for the Promotion of Science. NWRI internal report.

Onuska, F.I., Clement, R.E., Yang, F.J., Eiceman, G.A. and Hill, Jr., H.H. 1986. Gas chromatography-fundamental review. Analyt. Chem. 58: 321R.

Onuska, F.I. and Terry, A. 1986. Characterization and determination of PCB isomers by high resolution gas chromography and HRGC/mass spectrometry. J. High Resolut. Chromatogr. Chromatagr. Comm. 9:671-675.

Lawrence, J., Onuska, F.I., Wilkinson, R. and Afghan, B.K. 1986. Methods research: determination of dioxins in fish and sediments. Chemosphere 15 (9-12): 1085–1090.

In Situ Sediment Pollution by Heteroaromatic Compounds

F.I. Onuska, Study Leader

K. Terry

INTRODUCTION

This study is the continuation of the 1985/86 effort which was undertaken to develop a suitable methodology for nitrogen-containing polycyclic aromatic hydrocarbons in sediments. An evaluation of the effectiveness of the developed methodology on real samples of the Hamilton Harbour sediments was performed during 1986/87.

RESEARCH RESULTS

The first quantitative determinations of nitrogen-containing PAHs (azaarenes) in sediments are reported for the Hamilton Harbour cross-section consisting of 13 stations. Two- to four-ring azaarenes, in concentration as low as 2.0 ppb, are determined using high resolution gas chromatography with nitrogen-sensitive detection (thermionic detector) and by means of selective ion monitoring HRGC/mass spectrometry.

Azaarene distributions are locally and temporally variable. Their distribution in upper sediment layers suggests that total azaarene concentrations are related to proximity of industrial areas especially those closer to the coking-operations at the STELCO and DOFASCO plants. Possible azaarene inputs to the Hamilton Harbour include natural erosion of fossil hydrocarbon sources, such as coal, which is stored in large quantities on the shoreline, and combustion products, either directly in the form of deposition of air particulates or indirectly through stormwater or during preparation of coke in foundries. Weathering and other alterations of sedimented coal increase the extractable azaarene yield from coal matrices. High proportions of 3-ring azaarenes may be a general property of coal azaarenes.

Azaarene concentrations vary significantly in the relative amounts of the 2-ring and 3-ring azaarenes. GC/MS-spectra consisting of simple fragmentation patterns dominated by odd-mass parent molecular ions confirmed that most peaks identified by thermionic nitrogen detector were azaarenes, and provided isomer-specific information.

No previously unreported azaarenes could be identified in the samples, but identification of minor peaks was not possible due to non-nitrogen containing compounds in sediments dominating the GC/MS signal.

Proportions of different isomers vary widely between sediments. Surface sediments contained azaarene suites with fewer isomers of any size class, with greater numbers of quinoline and alkylquinoline isomers relative to benzoquinolines and azafluoranthenes.

The primary question which will be investigated in the final report is whether azaarene variations in sediments represent variations in different sources or variation within a single source, and whether azaarene data from the Hamilton Harbour are comparable to data in the geochemical and environmental literature.

In summary, 2-, 3-, and 4-ring azaarenes have µg/kg concentrations in sediments of the Hamilton Harbour grab samples. These measurements are the first of their kind in Canada. Area distributions of azaarenes suggest that their concentrations in upper sediment layers are related to proximity of industrial activities.

PUBLICATIONS

Onuska, F.I. and Davis, S. 1986. High efficiency open tubular column gas chromatography. Chromatogr. Jour., 1: 45–50.

Onuska, F.I., Terry, K. 1986. Characterization and determination of PCB isomers by HRGC and HRGCIMS. J. High Res. Chromatogr. Chromatogr. Comm. 9 (11): 671–675.

Preconcentration for Ultra-Trace Analysis

P.D. Goulden, Study Leader

D.H.J. Anthony

P.D. Goulden

INTRODUCTION

Many of the materials that are of environmental interest occur at levels that are too low for reliable measurement with conventional analytical methods. The route to improved sensitivity that has been pursued in a continuing program over several years is that of adding a preconcentration step to the front end of the analytical process. In some cases, this step can be tailored to separate the analytes of interest from the matrix, so that not only is the signal level enhanced, but also the signal-to-noise ratio is improved. This route has the advantage that it allows standard analytical instrumentation to be used for ultra-trace levels, and, with automation, it allows many samples to be measured on a routine basis in the National Water Quality Laboratory (NWQL). In the past, this route has been used for improved detection in the determination of metals by AAS and ICAP.

A study has been made of the feasibility of monitoring organics in water by sampling up to several hundred litres of water and extracting the organics with dichloromethane in a small continuous-flow, mixer-settler type of extractor. This has been shown to provide a valid preconcentration step for organics such as the organochlorines. When the solvent extract is obtained, it is then evaporated to small volume and a solvent-change is made for the cleanup procedures. Other evaporation and solvent-changes are made in the cleanup process. These evaporation processes have been difficult to carry out on a routine basis with conventional equipment, from a speed and convenience aspect and the fact that samples contain volatile analytes such as chlorobenzenes. A study has been made of the solvent fractionation process to overcome these difficulties.

RESEARCH RESULTS

With the new preconcentration and fractionation methods, extraction of most of the organics is complete. A number of different versions have been designed and used by the Water Quality Branch and the NWQL. These versions include:

1. Extractors to take a 50-L integrated sample over a 24-hour period. These are being used to monitor the Niagara River.

2. A prototype extractor to take a 100-L integrated sample over a 7-day period. This is automated and requires only that the stored sample be collected once per week. It has been operating on a trial basis at Niagara-on-the-Lake.

3. Extractors to sample water at 1-L per minute installed on board CSS *LIMNOS* to monitor the Great Lakes.

4. A 1-L per minute portable extractor used for one-at-a-site sampling of rivers and lakes.

In all of these extractors, surrogate standards are metered in with the water being sampled so that every sample has its own QA/QC assessment. in addition, a system has been developed for a second extraction of the effluent water so that the extraction efficiencies of the analytes can be accurately determined.

Another version of the extractor has been developed and is being tested. This is completely isolated from the atmosphere to reduce the exposure of the operator to dichloromethane vapors and to prevent contamination of the extract. It is believed that this version is suitable for use where gasoline engines are operated, such as in a small boat.

Distillation-fractionation systems have been developed that enable a rigid and valid separation of solvents and analytes to be made. Small-packed columns are jacketed so that water at the appropriate temperature can be circulated. There is an automatic reflux arrangement so that the distillation does not require 100% attention time. Studies were made to determine the efficiencies of the columns. A column having effectively three transfer

units is suitable for separations involving the volatile analytes such as the chlorobenzenes.

In support of the program on contaminated sediments, ways to analyze the "less-familiar" elements were investigated. It is found that determination by ICAP, using the previously developed heated spray chamber with desolvation technique provides a convenient and sensitive methodology. Approximate detection limits for 24 elements were determined. These elements are La, Ce, PN, Nd, Sm, Eu, Gd, Tb, Dy, Ho, EN, TM, Yb, Lu, Th, U, Be, Li, Sc, Y, Ta, Zn, Nb and Ti.

PUBLICATIONS

Anthony, D.H.J. and Goulden, P.D. 1986. Position coefficients of some Niagara River organic contaminants. NWRI Contribution 86-222.

Neilson, M., Stevens, R., Biberhofer, H., Goulden, P.D. and Anthony, D.H.J. A large-sample extractor for determining organic contaminants in the Great Lakes. IWD Technical Bulletin. In press.

Analysis for Organics in Dense Samples

B.F. Scott, Study Leader

J.F. Ryan

B.F. Scott

INTRODUCTION

The emphasis of this project is on, first, the qualitative and quantitative analysis for organic material, including sulfur containing compounds from dense matrices (sediments and extracts from large-volume extractors), and second, completing the methodology for phthalate esters (PAEs). Each part was requested by the National Water Quality Laboratory (NWQL). For all aspects, the analysis is performed using gas chromatography. Qualitative analysis requires, for each compound of interest, the absence of interference or masking by the other components in the sample. Interference can be reduced by altering either the cleanup procedure used or the gas chromatographic conditions. Quantitation depends on the chromatographic conditions as well as the interpretation of the signal obtained from the chromatograph. If the signal is not utilized correctly, the ultimate in cleanup procedures is of little value.

For analyzing extracts from dense media, we required the equipment to produce reproducible results, reintegrate values using adjusted parameters, provide a representation of the baseline, have internal calibration procedures, and control a number of instruments using different gas chromatographic programs. In addition, we needed the capability to utilize other mathematical techniques, such as pattern recognition procedures which can be used to identify complex mixtures extracted from dense matrices. This type of equipment is presently installed in the automated organic analysis facility of the NWQL, a major client of the Research and Applications Branch.

RESEARCH RESULTS

Toxaphene Determination

When the new high-speed injector methodology for toxaphene was being transferred into the NWQL, the reproducibility of the automated laboratory system was found to be poor, with a coefficient of variation greater than 5% for several of the components in toxaphene. We documented that there were several deficiencies in the equipment, both in the hardware and the software. These were resolved finally by the manufacturer. The new high-speed injectors could then be checked for reproducibility. It was found that for isothermal and programmed runs in split and splitless modes, the coefficient of variation was less than 5%, despite problems with solvent impurities and contamination from the sample vial septa.

We were then requested by the NWQL to provide a gas chromatographic method which would speed up the time of analysis for organochlorines (OCs) and halogenated benzenes, particularly for use in analyzing samples from the Niagara River. This was accomplished for a range of 33 compounds of interest, on a non polar column. Of the compounds, 24 have a coefficient of variation of less than 5% over a range of 0 to 1 pg/μL, as higher volumes caused peak distortion.

Once the gas chromatography was shown to properly quantitate compounds of interest, cleanup methodology was investigated for various OCs and sulfur containing compounds from sediments using HPLC. Since there is a paucity of information on organo-sulfur compounds in the aquatic environment, several compounds were selected for preliminary studies. These included endosulfan, α-chlordane, and several other OCs. It was determined that using a Sephadex column with CH_3Cl as the mobile phase, and a u-Porisil column with cyclohexane as the mobile phase, spikes of the above compounds could be recovered quantitatively.

Phthalate Esters Determination

A method for the determination of bis (2-ethylhexyl) phthalate (BEHP) and di-n-octylphthalate (DOP) in water samples in conjunction with the analysis of organochlorines was developed and reported. The method is compatible with the NWQL organochlorine residue analysis currently in use. The method incorporates the

qualitative analysis of BEHP and DOP into the NWQL analytical scheme for the analysis of organochlorines by a modification of the dichloromethane extraction and silica gel cleanup steps. This permits the simultaneous extraction of the phthalates and organochlorines from aqueous samples using dichloromethane and the contiguous elution of phthalate and organochlorine from silica gel cleanup columns for analysis by gas chromatography using electron capture detection.

A comparison of HPLC/UV and GC/ECD for the analysis of Hamilton Harbour water and sediment extracts revealed that conventional HPLC/UV methodology was unsuitable for quantitation of phthalate esters in environmental samples due to the non-specificity of the UV absorbance detector. It was found that phthalate ester contaminants cannot universally be removed from silica gel cleanup columns without seriously altering the elution pattern of the phthalates. Therefore, a normal phase HPLC/UV cleanup system was optimized for the removal of interfering organochlorines. The optimized HPLC cleanup system was evaluated using a variety of water and sediment extracts and found suitable for the cleanup of all six priority pollutant phthalate esters in complex matrices.

A gel permeation chromatography (GPC) system was optimized for the preliminary cleanup of sediment extracts and difficult water extracts. This GPC cleanup was found capable of removing the vast majority of the electron capture active coextractants present in sediment extracts as well as higher concentrated water extracts.

PUBLICATIONS

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Scott, B.F. and Ryan, J.F. 1986. Evaluation of methods for analyzing toxaphene in water and sediment. NWRI Contribution 86-99.

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Radioimmunoassay Technique for Dioxins

J.P. Sherry, Study Leader

R.J. Wilkinson

J.P. Sherry

INTRODUCTION

Conventional methods for the determination of PCDDs, which combine gas chromatography with mass spectrometry following extensive extraction and cleanup procedures, are extremely time-consuming and expensive when used for routine environmental monitoring. A gas chromatography mass spectrometry laboratory with two operators could be realistically expected to process a maximum of 10 samples a day, with an individual analysis including isomer confirmation costing between $500 and $1000. These are serious limitations when considered from the perspective of an environmental surveillance and monitoring program. The inclusion of an effective screening test in the analytical protocol for PCDDs could resolve some of the foregoing problems by eliminating those samples that are free of PCDD from further time-consuming conventional chemical analyses. Radioimmunoassay (RIA) has been suggested as a suitable screening technique.

RESEARCH RESULTS

1. A water soluble version of the RIA for PCDDs was developed using dimethylsulfoxide as the dioxin solubilization agent. The precision and sensitivity of the modified assay were determined to be superior to the original assay. Furthermore, the modified assay requires a 24-hour incubation period, as opposed to 72 hours in its original format. The modified assay was calibrated and standardized.

2. Five other solvents with similar characteristics to DMSO were also tested for possible use in the RIA for PCDDs; none was found to be suitable.

3. The stability of the radiolabelled dioxin derivative in DMSO was determined under various conditions.

4. The cross reactivities of 13 dioxin isomers in the RIA for PCDDs were determined. The octachloro congener failed to cross react, contrary to the published reports.

5. The cross reactivities of five PCDF isomers in the RIA for PCDDs were determined.

6. A critical experiment designed to determine the level of cleanup required for the analysis of lake trout samples in the RIA for PCDDs was carried out. The sample capacity of the assay was also examined.

7. A tyrosine-like derivative of TCDD was synthesized, labelled with I-125, and evaluated in the RIA. The information obtained is being used to synthesize an immunologically superior compound for use in an improved and safer labelling procedure.

8. The scientific literature pertaining to the use of immunoassays (RIA and enzymatic) has been surveyed, relevant articles have been obtained and perused and a feasibility report for management is in preparation.

PUBLICATIONS

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Sherry, J.P. 1986. Temporal distribution of faecal pollution indicators and opportunistic pathogens of a Lake Ontario bathing beach. J. Great Lakes Res. 12: 154-160.

Sherry, J.P. 1986. Temporal distribution of geoaquatic fungi at a nearshore station in Lake Ontario. J. Great Lakes Res. 12: 221–224.

Quality Assurance

A.S.Y. Chau, Project Chief

A.S.Y. Chau

SYNOPSIS

The mandate of the project is to ensure that chemical data generated for Environment Canada are of good and comparable quality. The project is essential for the successful management and utilization of water resources and for research on water pollution, especially the identification of spatial and temporal trends.

ISSUES AND RATIONALE

Environmental monitoring and assessment programs utilize large quantities of chemical analytical data from a variety of sources. These data must be of acceptable quality and comparable on a regional, national and international basis.

Stringent quality assurance protocols are essential for obtaining valid, precise and representative information about the environmental system under study. The procedures must ensure, and clearly demonstrate, the integrity of samples throughout collection, handling and analysis. Equally stringent procedures must be applied in the area of data management to ensure proper data utilization. Only by collecting and using data within specified tolerance limits can it be assured that spatial and temporal trends are statistically significant or that data from different laboratories are comparable.

Many of the advances in the field of quality assurance impact on the management of science rather than science itself. Expertise is a human, not a technical resource. Central quality assurance establishments gain in experience over time and provide unique insights, interpretations and advice.

For participating laboratories, the production of quality data involves the human elements of training, motivation, self-discipline and management. Central interlaboratory quality assurance programs accelerate progress up the learning curve and prevent backsliding. NWRI provides quality assurance support to over 190 federal, provincial, university and private sector labs.

PROJECT OBJECTIVES

As the responsibility center for quality assurance (QA), our objectives are:

1. to plan, coordinate and implement quality assurance and control programs to ensure accuracy, comparability and reliability of analytical data; and

2. to prepare and certify standard reference materials (water, sediments and biota) for use in interlaboratory comparison studies, intra-laboratory quality control activities and analytical method research.

PROGRAM

Project activities will include developing management plans for quality assurance, advising on field, laboratory and data management quality control procedures, preparing standard reference materials, conducting interlaboratory comparisons and conducting quality assurance audits.

Quality assurance studies will be conducted for federal, provincial, university and private laboratories producing analytical data for departmental programs (WQP, LRTAP, PPWB, GLWQP, federal-provincial Water Quality agreements). Methodology evaluation and sample preservation will also be carried out in support of these studies.

Within the Canadian scientific community, innovations in chemistry, biology and ecology have resulted in a wide range of tests and indicators of environmental quality. NWRI is establishing a program, in conjunction with the Cost Recoverable Technical Assistance Program at the Department of External Affairs, to marshall this valuable Canadian resource and market it effectively.

The new program will increase the market penetration of Canadian private sector environmental consultants and testing laboratories, by making a quality assurance program available on a cost recovery basis to Canadian companies bidding on contracts with domestic and international development programs.

In addition, marketing arrangements will be developed to make certified reference materials available to the private sector on a cost recovery basis.

CURRENT ACTIVITIES

1. Upper Great Lakes Connecting Channel Studies (UGLCCS). Develop quality assurance strategy and manage an interlaboratory QA program of 13 studies.

2. International Joint Commission (IJC) QA. Design and conduct four multi-level multi-sample interlaboratory studies (total P in water, organics in fish and sediment and metals in sediments).

3. LRTAP QA. Three multi-level, multi-sample interlaboratory studies for major ions and nutrients and for aluminum speciation.

4. Federal-Provincial Water Quality Monitoring Agreement QA Program and the Prairie Provinces Water Board (PPWB) QA Program. Design and conduct six bi-monthly studies for the PPWQ QA; a detailed integrated data evaluation on laboratory performance was also generated.

5. National QA. Design and conduct a national QA study for trace metals in sediment for data and methodology assessment.

6. Sample Stability and Preservation. Evaluate preservation techniques for PAHs, chlorobenzenes and phenoxy acid herbicides in natural water.

Quality Assurance (QA) Program - Upper Great Lakes Connecting Channels Studies

A.S.Y. Chau, Study Leader

W. Horn

INTRODUCTION

The Upper Great Lakes Connecting Channels Studies (UGLCCS) program was established as a bi-national study in late 1985. As progress continued through 1986, monitoring on the upper connecting channels continued with the purpose of defining the pollution controls necessary to establish a safe environment in this area. In order to ensure quality data are produced, the Quality Management Work Group (QMWG) was established by the UGLCCS and given the responsibility of developing a quality assurance program and conducting interlaboratory performance or quality control studies. As part of the QA program, the QMWG also develops detailed guidelines for other groups in their preparation of Work/QA project plans. These project plans define project objectives and field and laboratory quality control activities to be reviewed by the QMWG for completeness. This review greatly assists other work groups and also allows the UGLCCS program to achieve desirable data quality.

RESEARCH RESULTS

1. Two meetings of the Quality Management Work Group were held during 1986/87.

2. Seventeen Work/QA project plans from the sediment, point source, non-point source and water groups were reviewed.

3. Seven different interlaboratory quality control comparison studies were designed and distributed to the participating laboratories in the UGLCCS. These studies included a series of ampuls for constituents such as PCBs, PAHs and chlorinated hydrocarbons and insecticides. Other studies included mercury, cyanide and total phenol in water as well as chlorophenols in fish oils and tissues.

The interlaboratory study results reveal that, in general, the large service laboratories performed consistently better than the smaller service laboratories and that the research laboratories did not perform as well as the routine laboratories. The impact of these interlaboratory studies was clearly demonstrated. For instance, where ineffective in-house QC and instrumental calibration problems had resulted in severe analytical problems, the interlaboratory study was able to identify these problems and assist the laboratory in making corrections. These laboratories took immediate remedial actions and have drastically improved as reflected in later studies. Without these interlaboratory studies, these laboratories would not be aware of their internal analytical problems and would have continued to generate questionable data for the UGLCCS.

The Quality Management process was new to most participants. Project plans tended to follow the guidelines but were not necessarily complete in defining or justifying their methodology, data quality needs, or relationship to methodologies used by other related projects. There is a real need for agencies to recognize the importance of QA related documentation, and to be more prepared for external scrutiny in the future.

PUBLICATIONS

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QM-1: PCBs, OCs and CHs in ampuls, Final Report;
QM-2: PAHs in ampuls;
QM-3: Trace metals in sediments. Final Report.

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Organic Methods Development

Yvonne D. Stokker, Study Leader

H.B. Lee

Yvonne D. Stokker

INTRODUCTION

This study is part of the ongoing development of new and/or modified methods for the analysis and quantification of organic and biochemical parameters in a variety of substrates. These methods are designed to assist the National Water Quality Laboratory and regional Water Quality Branch laboratories in providing analytical data for a variety of programs and agencies.

More specifically, the goals for this project were:

1. to develop and validate a method for dinoseb analysis in sediments; and

2. to evaluate a mass selective detector (MSD).

RESEARCH RESULTS

Based on methods previously developed by this section for the analysis of chlorophenols, two GLC methods for the analysis of dinoseb in water and in sediment were established. These developments were extended to include the compounds bromoxynil, 3-trifluoromethyl-4-nitrophenol (TFM) and five other nitrophenols. Also, pentachlorophenol was added as an internal standard to monitor the relative extraction and derivatization efficiencies of each of the nitrophenols.

Preliminary work involved an in-depth comparison of the three procedures that formed the acetate, chloroacetate and pentafluorobenzyl ether derivatives of the nitrophenols. Following optimization of each of their respective reaction conditions, it was shown that acetylation was the method of choice for the nitrophenols by virtue of the ease of formation, extent of reaction and the stability of the products as well as their relative response to electron capture detection. Furthermore, it was shown that the applicability of this GLC analysis could be extended to include the 21 chlorophenol acetates, since the resolution of these compounds from the nitrophenol acetates was sufficient on a 12-m OV-1 fused silica capillary column for quantitation purposes.

The resultant method for the analysis of nitrophenols in sediment was successfully validated at two levels of fortification, with better than 90% recovery for each of the compounds of interest, using 50-g aliquots of Lake Superior and Battle River sediments. The practical limits of measurement range from 5 to 100 µg/kg.

In a similar method for the same parameters in water, validation data at three concentration levels were produced from fortified 1-L Lake Ontario water samples to a method detection limit of 0.025 µg/L for the mononitrophenols, and 0.010 µg/L for TFM, bromoxynil and the dinitrophenols.

Finally, a third "quick-and-easy" method, for the determination of dinoseb only, was also completed. This procedure involved the direct (*in situ*) acetylation of dinoseb in a 1-L water sample in the presence of potassium bicarbonate. The resultant acetate derivative was simultaneously extracted into an "injection-ready" organic extract. Using GC-ECD analysis, validation studies on both distilled and natural water samples provided better than 80% recovery at all three levels of fortification to a practical detection limit of 10 ng/L for a 1-L water sample.

Final reports on each of the above methods, including single operator statements on precision and accuracy, have been drawn up for inclusion in the WQB *Analytical Methods Manual*.

The MSD was set up for quantitative analysis of PAHs, chlorobenzenes and total PCBs by selective ion monitoring. The same detector was also successfully applied to the analysis of chlorophenol acetates in water and sediment samples (see Fig. 1). GC-MS spectral libraries for PAHs, chlorobenzenes and some pesticides as well as the derivatives of acid herbicides and phenols were created.

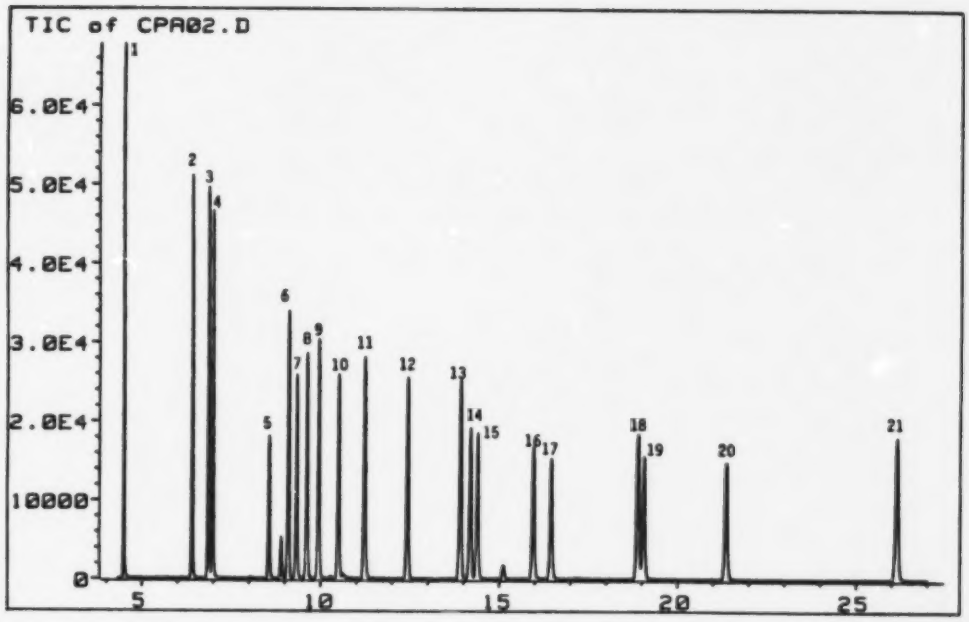

Figure 1. Total Ion Current Chromatogram of 21 Chlorophenol Acetates

PUBLICATIONS

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Pyrethroid Methods Development

H.B. Lee, Study Leader

A.S.Y. Chau

H.B. Lee

INTRODUCTION

Synthetic pyrethroids are insecticides already in use in many parts of Canada on fruits and vegetable crops for the control of pests. In order to study the fate and pathway of these pesticides, as well as their effects on surface and ground waters, it is necessary to develop sensitive and specific analytical methods for the determination of the parent pyrethroids and their major metabolites. The feasibility of several techniques that can be applied to the analysis of such compounds was evaluated.

RESEARCH RESULTS

The literature on the analytical methods currently available for the four synthetic pyrethroids was reviewed, namely: permethrin, cypermethrin, deltamethrin, and fenvalerate, as well as their major metabolites, 3-phenoxybenzyl alcohol (PBalc), 3-phenoxybenzyl aldehyde (PBald), 3-phenoxybenzoic acid (PBacid), and 3-(2,2-dibromovinyl)-2,2-dimethyl-cyclopropanecarboxylic acid (DBCA). Analytical standards of these compounds were acquired.

Chromatographic separation for a mixture of the parent pyrethroids was established with a 12-m OV-1 fused silica capillary column. Using a suitable temperature program, nine peaks were observed for the above mixture due to the presence of isomeric species. Two of them were attributed to permethrin (cis- and trans- isomers), four to cypermethrin, two to fenvalerate, and one to deltamethrin. Their electron capture detector response factors were also estimated.

Because of their low volatilities, very high column temperatures (above 260°) were required to chromatograph the parent compounds. When splitless injections were made on a capillary column, some memory effect due to carry over of the pyrethroids from one sample to the next was experienced.

A method for the analysis of the four synthetic pyrethroids in water at sub-ppb level was evaluated. This method involved solvent extraction of the pesticides by dichloromethane and the cleanup of the sample extract on a 10% deactivated Florisil column. Because of the relatively high polarity of these pesticides, the pyrethroids were eluted in the 1% acetone in hexane fraction. Quantitative recovery of the pyrethroids was obtained from water samples fortified at 0.3 to 0.5 μg/L levels. However, further work is required to evaluate the recovery of these compounds at even lower levels.

Another method for the analysis of the pyrethroid acidic metabolites, i.e., PBacid and DBCA was also developed. The acids were extracted from water by DCM after the sample was acidified to pH < 1. The extract was then derivatized into the ECD-sensitive pentaflourobenzyl esters in order to obtain the required sensitivity for the detection of a non-halogenated acid such as PBacid at low levels. The esters were further cleaned up on a 5% deactivated silica gel column before the toluene fraction was analyzed by ECD. Preliminary results indicated quantitative recovery of PBacid and DBCA at 0.5- to 0.7- μg/L levels. However, further evaluation of the method at other levels is required. Because of interference in the derivatized products, a GC-MSD method for the confirmation of products was also developed.

Two methods were evaluated for the analysis of the neutral metabolites, PBald and PBalc. One involved the HPLC technique using a reversed-phase C18 column for the separation of the metabolites and a variable wavelength UVD for quantitation. Although this combination was demonstrated to be sensitive (D.L. 50 ng/L), it was not specific or selective enough for the analysis of PBald and PBalc in natural water samples due to interference of coextractives. The other method involved the detection of these compounds using a capillary column interfaced to an MSD. By monitoring the molecular ions and a few characteristic ions, this highly selective method was also sensitive. Based on a concentration factor of 1000, the

detection limits for PBald and PBalc were 5 and 10 ng/L, respectively. Using DCM, extraction recoveries of these compounds were better than 85%.

These methods have been applied to the analysis of deltamethrin and its neutral and acidic metabolites in a number of samples collected in P.E.I. after spraying of the pesticides.

Further work is required to develop similar analytical methods for these compounds in sediment samples.

Preservation of Organics

H.B. Lee, Study Leader

N. Arafat and A.S.Y. Chau

INTRODUCTION

Since the centralization of Water Quality Laboratories across Canada, test samples are being shipped from the Atlantic, Quebec, Ontario, Western and Northern, and Pacific and Yukon regions to the National Water Quality Laboratory in Burlington for analysis. Frequently, samples will have to be stored for a period of time before extraction and analysis can be performed. In order to obtain meaningful results for the samples, their integrity must be maintained from the time of collection until the time of analysis. In many instances, information regarding the stability of organic parameters in water and sediment samples is lacking or incomplete. For the fiscal year 1986/87, the stability of chlorobenzenes, PAHs, and acid herbicides in preserved water samples was evaluated.

RESEARCH RESULTS

Regional water samples from British Columbia, Saskatchewan, Ontario, Quebec and New Brunswick were fortified with ten chlorobenzenes (di-, tri-, tetra-, penta-, and hexa-chlorobenzene), hexachlorobutadiene, and octachlorostyrene, together with 16 PAHs listed in U.S. EPA Method 610. The levels of fortification in this study are between 50 and 1000 ng/L for the chlorinated compounds and 1 µg/L for all PAHs. After fortification, each water sample was stirred with 10 mL of chloroform for 10 minutes and immediately stored at 4°C in the dark. Replicate samples were removed and analyzed for chlorobenzenes and PAHs immediately after spiking, and after 3, 6, 9, 12, and 15 weeks of storage. All samples were extracted and cleaned up according to the multi-residue procedure developed earlier (NWRI Contribution 86-88). The final analyses of chlorobenzenes were done by GC-ECD and PAHs by GC-FID, using suitable capillary columns.

Results indicated that the chlorobenzenes in the preserved water samples were stable over the study period. Average recoveries were better than 80% in most cases. Other than some random fluctuation in recoveries due to experimental errors, there was no continuous decline in chlorobenzene concentration to suggest degradation. Recovery of PAHs in the preserved water sample was usually better than 85% except for the following cases. Recovery of the more volatile PAH such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, and anthracene were low and erratic. Therefore, another study is being repeated to ascertain the stability of the above six PAHs. Recovery of PAH from the fortified New Brunswick water was also lower than the other waters due to the formation of emulsion during the extraction steps. Nevertheless, the overall results suggested that the 10 less volatile PAHs were stable in the preserved water samples.

In another study, regional water samples fortified with the 10 acid herbicides analyzed by WQNL were preserved with 5 mL of 1+1 sulfuric acid (pH < 1). The levels of fortification were between 0.1 and 0.2 µg/L. Replicate samples were then analyzed at 0-time, as well as 5, 10, and 15 weeks after spiking. The analyses are near completion and the results are being evaluated.

PUBLICATIONS

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Development of Organic Certified Reference Materials (CRMs) and National Quality Assurance

H.B. Lee, Study Leader

Y.D. Stokker, V. Cheam and A.S.Y. Chau

INTRODUCTION

The major goals for this study were to develop CRMs for organic parameters such as PCB, PAH and chlorobenzenes, and to implement interlaboratory studies on organics for the national and Federal Interdepartmental Committee on Pesticides (FICP) programs. Extensive service was also provided for the organic studies in the IJC and Upper Great Lakes Connecting Channels (UGLCC) QA programs. Also included for this fiscal year was the implementation of a national QA study for toxic trace metals in sediments.

RESEARCH RESULTS

GC-MS and HPLC analyses were performed for the PAHs in two new sediment reference materials, namely, EC-4 and EC-5. Results for the 14 PAHs in each material were summarized and evaluated. The same CRMs were also screened for chlorobenzenes. Since only insignificant amounts of these compounds were found, no further development work was done. Results from several interlaboratory studies involving PAH sediment CRMs were also compiled and analyzed. These interlaboratory results together with in-house data are being used to generate certified or reference values for PAHs in CRM EC-1 through EC-5.

A procedure was designed for the homogeneous mixing of primary sediment CRMs to produce subsamples of secondary sediment CRMs for organics. Using this technique, three blended sediments were prepared and analyzed for their PCB, chlorobenzene and PAH content. Five sediment CRMs were screened for 21 chlorophenols using the analytical method developed in 1985/86. The results of these tests indicated the presence of some of the chlorophenols in each sediment, including pentachlorophenol, at or near the method detection limit.

A national QA study for trace metal analysis in sediments was completed. A final report was prepared and distributed to about 40 participants. An FICP study for triazine analysis in water was completed. A data summary has been generated and the information forwarded to the chairman of the FICP Check Sample Program. A special study for chlorophenol analysis in fish and related materials was also implemented for the labs involved in analyzing samples from Fraser River Estuary. The results of this study indicated that comparable and reproducible data were obtained from the participants for pentachlorophenol and 2,3,4,6-tetrachlorophenol in the naturally contaminated fish samples. Results for 2,4,6- and 2,3,6-trichlorophenols were, however, more divergent. Erratic in-house standard solutions were likely to be the major source of analytical error in this study. A final report was distributed to the participants.

To support the Great Lakes Surveillance QA program, ampuls and sediment test samples were prepared for IJC Study 52, Parts I, II, and III (analysis of PCBs, organochlorine insecticides, and PAHs). In preparation of future interlaboratory studies for organics in fish, preliminary results for the lipid, PCB, and OC contents in ten fish reference samples were obtained by in-house analysis. Continuing support in terms of study design, sample preparation, data interpretation and report writing was also given to the UGLCC program.

PUBLICATIONS

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Cheam, V., Chau, A.S.Y. and Horn, W. 1986. National interlaboratory quality control study No. 35—Trace metals in sediments. NWRI Contribution 86-223.

Inorganic Methods Development and the National Interlaboratory Quality Control Study

V. Cheam, Study Leader

A.S.Y. Chau

V. Cheam

INTRODUCTION

This study comprises two key activities of the inorganic quality assurance program: the method development and the National Interlaboratory Quality Control (QC) study. The method component develops and validates analytical methods for routine use by regional and national Water Quality laboratories. The National QC study serves:

1. to assess methodology and data of the Water Quality laboratories by comparison with peer laboratories;
2. to establish laboratory performance of federal, provincial, university and private laboratories; and
3. to provide additional data for certification of reference materials.

RESEARCH RESULTS

For the first time, an ion chromatographic method has been successfully developed and validated for the simultaneous analysis of the three groups of major ions—anions and monovalent and divalent cations. Twelve such ions, Li^+, Na^+, NH_4^+, K^+, Mg^{++}, Ca^{++}, F^-, Cl^-, $HPO_4^=$, NO_2^-, NO_3^-, and $SO_4^=$, can be simultaneously analyzed. Overall, the method is more sensitive and more cost effective than the conventional methods, in which each of the ions has to be analyzed separately using atomic absorption, flame photometry and colorimetry. The method is also versatile in that it can operate as an independent anion system, monovalent system, divalent system, or a joint system with any combination the analyst desires.

The National Interlaboratory Quality Control Study No. 35, trace metals in sediments, forms an integral part of the continuing Quality Assurance Project at NWRI. It dealt with the analysis of ten heavy metals in five different sediment reference materials. Some 50 Canadian laboratories participated in the study, many of which reported compatible heavy metals data although a few laboratories tended to have consistently biased results. The "total" content was greater than the "extractable" content for each of the metals studied. The "total"/"extractable" ratio varied from metal to metal and ranged from 3.5 for Al to 1.02 for Cu.

PUBLICATIONS

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IJC Quality Control (Interlaboratory Studies)

K.I. Aspila, Study Leader

K.I. Aspila

INTRODUCTION

Interlaboratory quality control comparison studies are provided to laboratories in response to the Canada-U.S. Great Lakes Water Quality Agreement and in support of the International Great Lakes Surveillance Work Group. These studies are evaluated to identify comparability of agency data and problems associated with the laboratory measurement process. Comparable data of high quality are essential if the agencies and jurisdictions are to merge data bases to define trends in pollutant concentrations, loading estimates, and compliance with water quality objectives, or to respond to remedial measures.

Studies involve a mixture of natural and synthetic substrates. Results for laboratory data sets are interpreted for measurement bias by the rank-order method of Youden. Results on individual samples are flagged high or low when they deviate significantly from interlaboratory median values. When studies are completed, performance appraisals are provided to each laboratory head and pertinent managers. The distribution of laboratory appraisals now includes members of the Water Quality Board.

In 1985, the data evaluation process was expanded to include graphics and a more powerful process to discern bias using the Wilcoxan rank sum techniques.

This ongoing project addressed several interlaboratory comparison studies. They are listed below.

1. Toxic Organics in Ampuls

   This study involved 40 laboratories which were provided ampuls of injection-ready standards (PCBs, PAHs and chlorinated hydrocarbon pesticides). The study was initiated in January 1986 and completed in August 1986.

2. Toxic Organics in Sediments - PCBs and OCs

   This study included eight reference sediments and three ampuls. It was distributed to 37 laboratories in March 1986 and was completed in April 1987.

3. PAHs in Sediments

   This study included eight reference sediments and two ampuls. It was distributed to 27 laboratories in March 1986 and was completed in April 1987.

4. Toxic Organics in Whole Fish Homogenates

   This study, although scheduled for 1987, has been deferred to a later date since the disappointing results of two other studies clearly indicate laboratories need to improve calibration procedures. A new study on ampul standards is being scheduled for 1987/88.

5. Total Phosphorus in Water (Low Levels)

   This study included 15 aqueous test samples and was distributed to 26 laboratories in July 1986. The study was completed in January 1987.

6. Toxic Organics and Inorganics in Sediments

   Several hundred kilograms of wet bottom sediment from Lake Erie and Lake St. Clair have been collected. These were freeze-dried, crushed, screened, homogenized and bottled. These materials (10 different sediments) will be used in 1987/88 as reference materials for two new studies.

7. Total Phosphorus in Sewage Treatment Plant Effluents

   This study involved 82 laboratories within the Great Lakes Basin that routinely analyze phosphorus in sewage effluents. The study was distributed in January 1987 and evaluated in April 1987.

RESEARCH RESULTS

These studies have very clearly informed analysts and their management structure on their performance. Although some laboratories are clearly satisfactory, a few (perhaps 15% to 25% within a study) have serious bias or were very erratic (serious imprecision). The users of data must remain vigilant and review all performance appraisals relative to their project objectives and establish closer liaison with their laboratories.

The primary source of variability between laboratories was differences in calibration standards. This issue will be addressed in future studies.

The phosphorus in sewage study was again a disappointment as it clearly revealed that many laboratories (perhaps 25) have major problems in estimating total phosphorus. A poor estimate by laboratories means phosphorus loading estimates to the Great Lakes are of questionable quality.

PUBLICATIONS

Laboratory specific appraisals for all studies are on file in the IJC Great Lakes Regional Office for review on a need-to-know basis.

LRTAP Interlaboratory Quality Control Studies Aqueous Phase

K.I. Aspila, Study Leader

P. Leishman and A.S.Y. Chau

INTRODUCTION

This project supports the Federal-Provincial Research and Monitoring Coordinating Committee Quality Assurance Subgroup. It is designed to define and improve the quality of data generated by laboratories participating in LRTAP.

This ongoing project provides three interlaboratory comparison studies each year to laboratories that analyze aqueous samples in support of the federal-provincial LRTAP. The three studies are identified in Table 1.

Results of interlaboratory data were appraised for bias by the non-parametric rank order method of Youden. Individual sample results deviating significantly from interlaboratory medians were flagged either high or low. Information on very low frequencies of bias and flags, over several studies, has allowed some labs to be categorized as satisfactory. A few laboratories, very frequently flagged and very frequently biased, are considererd poor in these peer group appraisals.

Studies were distributed and completed within 16 weeks, during which time, each participant was provided a laboratory specific performance appraisal. If appraisals were poor the participant was expected to take corrective action. Formal study reports for distribution through the LRTAP Liaison Office are prepared afterwards.

RESEARCH RESULTS

Work continues on the following:

1. the preparation of reference water specific to the LRTAP program;
2. refinement and expansion of existing computer programs;
3. analysis of the stability and homogeneity of reference waters; and
4. liaison with analysts, managers and users of LRTAP data.

Table 1. Summary of Studies

Study No.	Distr. of Study	Closing Date	Design	No. of Samples	No. of Participants Expected	No of Participants with data
L12	Apr. 86	July 86	Major Ions	10	48	44
L13	June 86	Aug. 86	Aluminum (total and speciation)	22	19	19
L14	Dec. 86	Mar. 87	Major Ions	10	53	45

This interlaboratory program is viewed as a very constructive program that improves the quality of data through peer group comparisons. In each study about 10% to 20% of the participants are identified as either erratic, out of control or significantly biased. Several such laboratories are now satisfactory, and it is believed that as the program continues further improvements will be made.

PUBLICATIONS

Summary reports to each laboratory have been provided in a timely manner. Formal reports for each study have been prepared and are available through the LRTAP Liaison Office.

Federal-Provincial and PPWB Quality Assurance Programs

H. Alkema, Study Leader

H. Alkema

INTRODUCTION

Under terms of the federal-provincial agreements and the agreements under the Prairie Province Water Board (PPWB), these quality assurance programs are designed to assess and improve the comparability of water quality data.

These programs provide bimonthly studies for some 40 inorganic constituents in surface waters, for 12 federal and provincial laboratories. A laboratory in the Indian and Northern Affairs Program also participates in these programs.

Each bimonthly study provides for quick data evaluation within several weeks. Data are tested in absolute terms with the use of certified reference waters. Generally, laboratories report their data in a timely manner and take corrective action when data are identified as anomalous.

In addition to quick turn-around evaluations, the PPWB requests long-term data assessment for comparability of data. Computer programs are continually modified to meet their requests for precision and accuracy reports.

Complete summary reports, provided bimonthly to laboratory heads and their superiors, outline the study design and data evaluations. The annual compiled reports listed below contain six of these reports.

RESEARCH RESULTS

Work continues on the following:

1. preparation and development of certified reference waters for the PPWB long-term data assessment;
2. planning and development of an automated computer assessment process for short- and long-term data evaluation;
3. redesigning of the long-term data base for data retrieval, data evaluation and graphic presentation.

These interlaboratory QA programs improve the performance of the laboratory measurement systems. Performance is checked by the laboratories' ability to achieve target levels for certified reference samples. Good performance is recognized if the laboratories achieve these target levels and consequently have few anomalies in their data. Several laboratories have reduced their number of anomalies and thus have shown improvement in their data quality.

PUBLICATIONS

Alkema, H. 1986. Summary report PPQC studies 25-36 (Sept. 84–Aug. 85). NWRI Contribution 86-89.

Alkema, H. 1986. Summary report IRQC studies 120-131 (Sept. 84–Aug. 85). NWRI Contribution 86-90.

Alkema, H. 1986. Summary report PPQC studies 37-48 (Sept. 85–Aug. 86). NWRI Contribution 86-170.

Alkema, H. 1986. Summary report IRQC studies 132-143 (Sept. 85–Aug. 86). NWRI Contribution 86-171.

Alkema, H. 1986. Rapport sommaire PAQFP 1-6 (Juillet 85–Juin 86). Collection INRE 86-177.

Hydraulics Studies

M.G. Skafel, Project Chief

M.G. Skafel

SYNOPSIS

The mandate of the project is to advance knowledge and to provide expertise and support on the dynamics of water and its interactions with the air, shores, and river and lake beds. The output of the project supports the management of water resources directly through its research in river and sediment metrology, in the transfer of pollutants across the air-water interface, in the energy transfer between air and water, and in the generation and propagation of waves and their interactions with shorelines, and indirectly by providing a framework for aquatic biology and chemistry research. Access to its expertise and hydraulics laboratory facilities is being maximized through the development of marketing strategies.

ISSUES AND RATIONALE

To make informed decisions, water resource managers require an understanding of the interaction of water with air and with the sediment and shores in lakes, rivers, diversion systems and on coasts. Scientifically sound and up-to-date methods of flow and sediment transport measurements are vital to successful monitoring of water resources and the pollutants in sediment. Knowledge of the rates of transfer of pollutants between water and the atmosphere is needed to evaluate the significance of "toxic rain" on the quality of lake water.

Management of water resources in lakes and coastal regions must be founded on knowledge of the interactions of the water with its boundaries. Surface waves play a dominant role at the air-water boundary where wind energy is transferred to the water.

New knowledge is required to address the issue of resuspension and transport, primarily by wave action, of polluted bottom sediments. Shore erosion and the integrity of shore structures are issues of particular concern during periods of high water levels on the Great Lakes.

Increased environmental concerns and the high cost of water resource developments demand the best possible planning. Reliable predictions of the effects of proposed water projects require computer simulation models with firm scientific foundations.

New technological developments must continue to serve the dual public interest of economic prosperity and overall quality of life over the long term. Technological development can only be sustained if economic and environmental factors are considered together at the planning stage of technological innovation.

As a pilot project, the Hydraulics Laboratory is adapting the generic five-point strategy for science of the Ministry of State for Science and Technology Canada (MOSST) to meet the challenge of sustainable development:

1. develop intellectual capital (center of expertise);
2. develop new knowledge and technologies relevant to priority issues (directed research);
3. support industrial innovation and technology diffusion (technology transfer);
4. strengthen the impact of federal research and development (marketing);
5. develop an informed public (science communication).

By making first-class expertise and facilities accessible, environmental and economic forecasting become more predictable and legitimate; entrepreneurs in the economic sector recognize (and realize) the advantages of sound environmental planning, environmental considerations are included in the decisions made by private enterprise, and environmental industries grow.

PROJECT OBJECTIVES

To develop expertise and knowledge in wave mechanics and in coastal and fluvial engineering and to communicate new scientific findings developed at NWRI and elsewhere to managers and engineers in Environment Canada, clients, Canadian water managers, and the scientific community at large.

To produce theories, methods and models that will permit reliable analyses and predictions of the physical effects relating to natural processes or human intervention in rivers and lakes.

To operate the Hydraulics Laboratory in an efficient and effective manner, and to provide technical support to scientists using the facilities.

To respond to client requests consistent with longer term strategic research, and to develop policies and programs that will increase the use of laboratories where the equipment is not readily available elsewhere, particularly in the private sector.

RESEARCH PROGRAM

The research program in wave mechanics creates new knowledge of the accurate parameterization of fluxes of mass, momentum, energy and heat across the air-water interface. This work has direct consequences in understanding toxic gas transfer, diffusion of pollutants, wave prediction, lake circulation, seasonal thermocline development, weather forecasting and climatic change.

The coastal engineering program addresses the questions of bottom interactions such as the resuspension of cohesive (polluted) sediments by waves, hindcasting techniques used to develop climatic data on sediment resuspension and shoreline evolution, and wave-structure interaction especially in regard to situations where structural failure could lead to serious environmental consequences.

The fluvial engineering program is directed at improved understanding of the fluid mechanics and sediment transport of rivers and the development of new and improved techniques for monitoring river processes. Emphasis is placed on providing information for operational branches in Environment Canada. Results are often applicable to issues in other departments and to other water resource managers.

CURRENT ACTIVITIES

Wave Mechanics

A new wind-wave flume is being prepared to examine the mechanisms of toxic gas transfer at the air-water interface. The analysis of Lake St. Clair wave data is being completed and the new findings will be incorporated into the NWRI wave prediction model. The final phase of the field measurements addressing the topics of wave orbital velocities, turbulence and mixing in a whitecapping sea will be completed and analysis of the data continued. Analysis of field and laboratory data will continue aimed at elucidating the mechanisms for transfer of mass, momentum and energy between air and water. Theoretical analysis of the energy balance of wind waves and the implications for satellite remote sensing continues.

Coastal Engineering

Data on the wave resuspension of Lake St. Clair bottom sediment are being analyzed and incorporated into a model for resuspension of cohesive sediment. The impact of a new breakwater at Goderich on the littoral processes is being assessed. Field experiments to verify a procedure to obtain the joint distribution of wave heights and periods in shoaling water will be conducted. The two-dimensional NWRI wave prediction model will be incorporated into a wave climate model and this technology transferred to the private sector. Validation of pressure transducer techniques for wave measurement will be done, using field data.

Fluvial Engineering

Applied research is being conducted in support of Water Resources Branch programs. The evaluation of discharge measurement schemes for the Milk River will be completed. Optimum sampling procedures for bed load measurements will be determined and dune dynamics will be defined. The effect of turbulence on current meter response will be documented. A reliable method of measuring river flow for irregular bed profiles will be established. A prediction procedure for the critical shear stress for non-uniform grain size bed material will be developed. Applied research is also being conducted on streambed erosion protection in cooperation with the private sector.

Marketing

In 1987/88 Environment Canada jointly with Treasury Board is contracting the services of expert consultants to explore marketing strategies for the Hydraulics Laboratory

and new arrangements with the private sector to facilitate private sector access to this national center of expertise.

Technical Services

The technical staff operate the facilities in the hydraulics, sedimentology and geotechnical laboratories and provide specialized support to the professional users of the laboratories on an ongoing basis and to cost recovery projects. The National Calibration Service Unit calibrates and repairs current meters and operates the towing tank facility for the Institute, Water Resources Branch, and users in the private sector. New equipment is being incorporated into the operation of the laboratories: a new settling tube for sediment size analysis and a new microcomputer-based data acquisition system for the wind-wave flume.

Air-Water Interactions

M.A. Donelan, Study Leader

C. Bishop, D.C. Beesley, I. Tsanis (NSERC Visiting Fellow), WHOI Staff, and U.S. NRL Staff

M.A. Donelan

INTRODUCTION

This study formed the second phase of a three-year field study of breaking waves and wave-turbulence interactions. The observations were made on NWRI's research tower in Lake Ontario by a team of researchers from NWRI, the Woods Hole Oceanographic Institution (WHOI), and the U.S. Naval Research Laboratory (NRL). This complex experiment involved three dozen instruments and almost 100 recorded signals. The central goal was to investigate the velocity structure beneath breaking waves by means of fast response velocity-measuring instruments arranged in a vertical array on the west side of the tower. The array could be rotated to optimize the exposure of the instruments to the wave-induced velocities.

RESEARCH RESULTS

The analysis of four representative cases, covering the range of swell with no wind to very strongly forced fetch-limited waves, was completed and reported to the ESRF Workshop on wave hindcasting and forecasting in Halifax, September 1986. Figure 2 is a set of time series of measured surface displacement and velocity for conditions of strong winds at short fetch so that wave breaking is widespread.

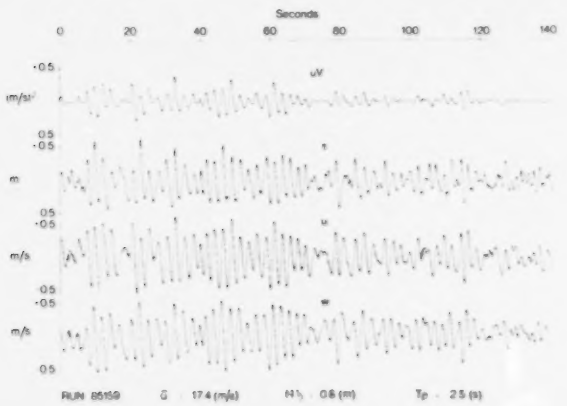


Figure 2. A section of the time series of the measured surface elevation η, horizontal (u) and vertical (w) velocity components at 1.25 m depth. The top curve (uV) is the instantaneous product of the horizontal velocity and the magnitude of velocity vector. This figure is drawn from a case of strongly wind-generated or very underdeveloped conditions.

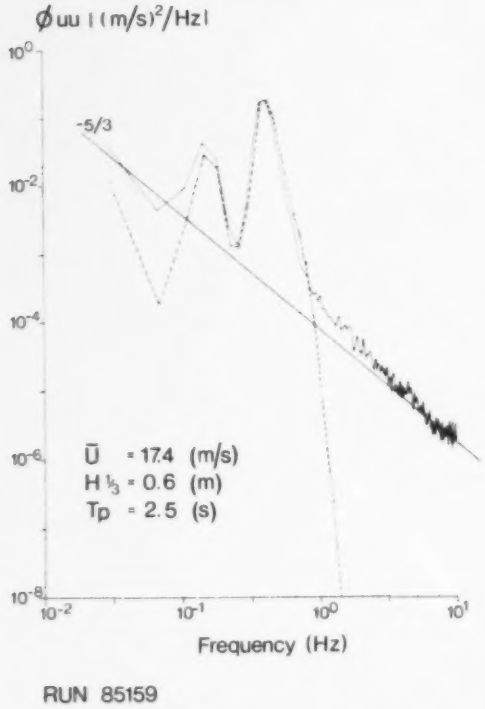


Figure 3. The spectrum of horizontal velocity for the case of strongly generated waves. The solid line is for measured horizontal velocity and the dotted line is the calculated spectrum from the spectrum of surface elevation through linear long-crested theory. The -5/3 line shown corresponds to the inertial sub-range of isotropic turbulence.

The spectrum of horizontal velocity (Fig. 3), corresponding to the time series of Figure 2, indicates a well-developed inertial sub-range and substantial differences from linear theory. Further analysis is proceeding to deter-

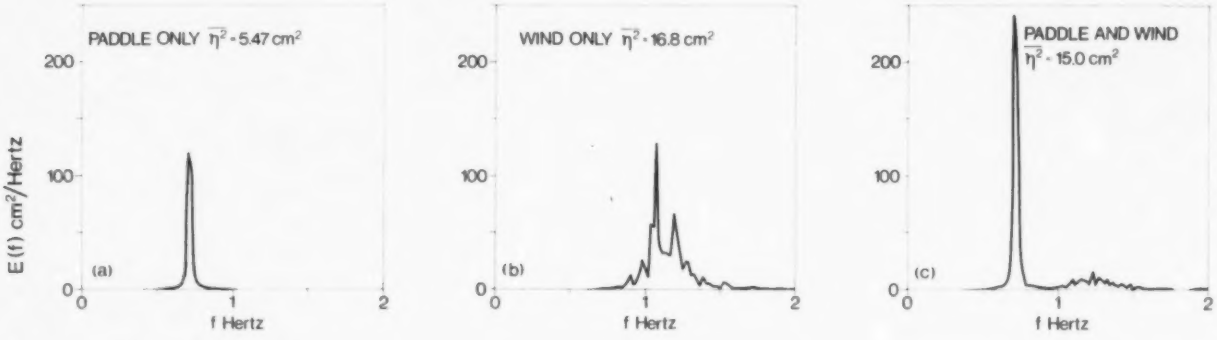
mine a suitable description of velocity statistics beneath breaking waves that will provide a better guide to design of offshore structures than the present reliance on linear theory.

These data are also being analyzed to explore the interaction of waves and turbulence in a breaking wave field and to estimate the level of energy dissipation. This part of the investigation (with WHOI) is expected to yield useful insight into such phenomena as upper mixed layer dispersing, pollutant dispersal near the surface and gas transfer across the interface.

A third aspect of this work (with NRL) deals with the measurement of the microwave reflectivity of a wind-roughened surface and its dependence on water temperature, wind speed and wind direction relative to the pointing direction of the radar. Three radar frequencies were used corresponding to wavelengths in the range of 5 mm to 5 cm. The response of waves of these wavelengths to wind is at the heart of measuring ocean winds from space with scatterometers, and this work will help provide a sounder basis for the analysis of such data.

The final component of this study concerned the measurement of pressure and velocity near the surface in order to estimate the exchange of energy between waves and wind. This is an important consideration in the numerical prediction of sea state and will influence the new generation of wave models being developed for global wave prediction.

One of the most intriguing aspects of the growth of wind waves is the striking difference in growth rates observed in the presence of laboratory "swell" (i.e., low frequency paddle-generated waves) as shown in Figure 4. Laboratory data were analyzed to see if the difference in growth rate is due to a direct modification of the momentum input to the wind-waves in the presence of swell. It was found that this was not the case, and it was further deduced that the most likely source of the difference arises in the de-tuning of the weak non-linear interactions among the wind-waves when there is swell present to alter the dispersion relation. This work was presented at the Symposium on Measuring Ocean Waves from Space at the Applied Physics Laboratory of the Johns Hopkins University, Baltimore, Md. in April 1987.



Panel (a): Spectrum of a continuous train of 0.707 Hz paddle-generated waves of steepness ak = 0.067.

(b): Spectrum of a pure wind sea with measured wind of 11 m/s at 26 cm height.

(c): Spectrum of waves with wind and paddle excited together as in (a) and (b).

Figure 4. Wave spectra at 50 m fetch in a laboratory wind-wave tank.

PUBLICATIONS

Donelan, M.A. and Pierson, Jr., W.J. 1986. A two-scale bragg scattering model for microwave backscatter from wind generated waves. NWRI Contribution 86-110. Proceedings of IGARSS '86 Symposium, Zurich, Sept. 8-11, 1986. Ref. ESA-SP-254, 291–296.

Pierson, Jr., W.J. and Donelan, M.A. 1986. Verification results for a two-scale model of microwave backscatter from the sea surface. NWRI Contribution 86-111. Proceedings of IGARSS '86 Symposium, Zurich, Sept. 8-11. Ref. ESA-SP-254, 297–302.

Donelan, M.A. 1987. The effect of swell on the growth of wind-waves. NWRI Contribution 86-117. Published in the John Hopkins APL Technical Digest, Jan.-March, Vol. 8, no. 1.

Donelan, M.A. and Kahma, K.K. 1986. Observations and velocities beneath wind-driven waves. NWRI Contribution 86-120. Proceedings of the International Workshop on Wave Hindcasting and Forecasting, Halifax, N.S., September 23-26, 1986, 243-252.

Waves and Bottom Interaction

M.A. Donelan, Study Leader

M.G. Skafel and D. Beesley

INTRODUCTION

Shallow water wave modelling hinges to a considerable extent on appropriate specifications of the interaction of the waves with the bottom. This study was set up to explore wave-bottom interactions in Lake St. Clair. This, the smallest of the Great Lakes, is particularly suitable for such studies because it is relatively shallow (average depth about 5.5 m) and very flat-bottomed. The experiment consists of the measurement of frequency spectra and frequency-direction spectra on six towers arranged as in Figure 5. Transmissivity was measured at one tower concurrently with wave measurements to investigate the influence of the waves on the resuspension of bottom sediments.

RESEARCH RESULTS

A considerable body of data was collected in the fall of 1985 and the analysis is being conducted by scientists from NWRI, NOAA (GLERL), AES and WHOI. Important changes in spectral shape and growth rates have been observed in cases of strong northwest winds, and these are being compared with equivalent deep water measurements. Pronounced deviations of peak wave direction from the wind direction have been noted and observed to follow the similarity theory established by Donelan *et al* (1985) on the basis of Lake Ontario measurements.

Time series of transmissivity and waves were collected over a period of three months. Low values of transmissivity correlated well with extreme wave conditions, but there was poor correlation with several intermediate intensity events. Bottom surficial sediment at the site has a wide particle size range, so several ways were examined of establishing the calibration to determine quantitative values of suspended sediment. Laboratory tests were done to examine resuspension of the sediment by paddle-generated waves. Resuspension was dependent on the history of the previous tests as well as contemporary conditions. Analysis is continuing.

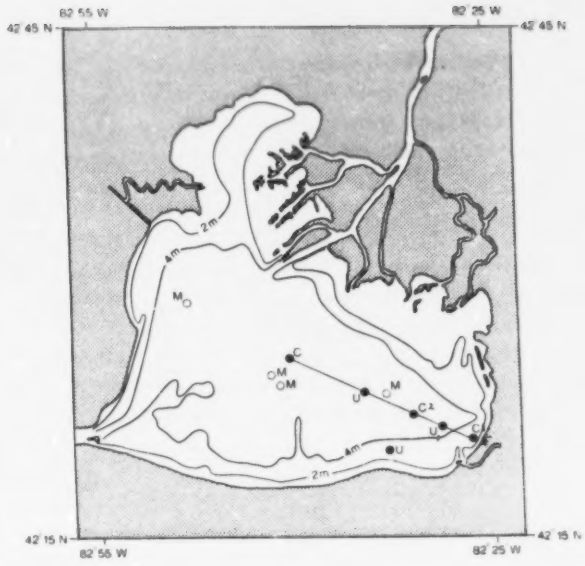


Figure 5. Waves and bottom interaction. Tower (•) and buoy (°) sites in Lake St. Clair.

PUBLICATIONS

Skafel, M.G. 1986. On the calibration of transmissometers. NWRI Contribution 86-115.

REFERENCES

Donelan, M.A., Hamilton, J. and Hui, W.H. 1985. Directional spectra of wind-generated waves. Phil. Trans. R. Soc. London A315, 509-562.

Transfer of Toxic Gases

M.A. Donelan, Study Leader

N. Merzi (NSERC Visiting Fellow)

INTRODUCTION

A comprehensive literature survey of gas transfer theory and measurements has been conducted and is being summarized as a technical report. A closed wind tunnel, to be added to the 32 m x 0.6 m x 0.4 m flume, has been designed and specifications are being prepared in preparation for its construction. It is expected that the new gas transfer wind-wave tunnel will be ready for use in early 1988.

Measuring Waves with Pressure Transducers

C. T. Bishop, Study Leader

M. A. Donelan

C.T. Bishop

INTRODUCTION

Although the measurement of waves with pressure transducers has been practised since around 1947, there still remain considerable differences in findings on the adequacy of linear wave theory to compensate the pressure records. Measurements of surface elevation in gravity waves are compared with corresponding estimates from simultaneous subsurface pressure measurements. A review of previous work precedes a description of laboratory tests in a 103-m long wave flume at Canada's National Water Research Institute. Pressure transducers and surface-piercing capacitance wave probes are used to collect data in water depths of 0.9 and 1.2 m with monochromatic and irregular waves.

RESEARCH RESULTS

There is now considerable information affirming that linear wave theory is adequate to compensate pressure data and give reliable estimates of surface wave heights. A well-designed pressure transducer system with proper analysis techniques should give estimates of surface wave heights accurate to within ±5%. In designing such a system, the pressure signal to noise ratio must be given careful consideration, and, if necessary, be compensated. Only spectral analysis of the data, not a wave-by-wave analysis, will give adequate results. When measuring waves with pressure transducers in shallow water the linear theory pressure response factor may require modification to account for currents or wave non-linearity.

Previous results, which indicate that linear theory requires a substantial correction factor N to adequately compensate pressure records, probably suffer from one or more of the following:

- inaccurate measurement of surface wave heights (including meniscus errors);
- instrument limitations (including signal to noise ratio, calibration error or drifting, hydrodynamic noise);
- analysis methods (including wave-by-wave method, spectral leakage).

PUBLICATIONS

Bishop, C.T. and Donelan, M.A. 1986. Measuring waves with pressure transducers. NWRI Contribution 86-124. Coastal Engineering. In press.

Wave Prediction Models

C. T. Bishop, Study Leader

M. A. Donelan and M. G. Skafel

INTRODUCTION

At the request of an editor of a forthcoming book on coastal modelling, a chapter on wave prediction models was prepared. Subsequently, an intercomparison of several wave hindcast models was initiated. For design of coastal works and for studies into shoreline erosion and sedimentation problems, it is necessary to have a good understanding of the local wave climate. Typically, measured wave data, if available at all, is only of very limited duration. Engineers must resort to modelling the wave climate, and normally make use of steady state wave hindcasting models incorporated into a computer program to use in time series mode. Several models are compared for locations in western Lake Ontario. Existing models used by Public Works Canada and several Canadian consulting engineers and a modified version incorporating wave direction are used.

RESEARCH RESULTS

A review of state-of-the-art wave prediction models was prepared. The following topics were covered: empirical models (SMB, JONSWAP, Donelan), wave climate models, wave refraction and shoaling, TMA spectrum, numerical models (discrete spectral, parametric).

The empirical models predict single value estimates of locally generated wave height and period in deep water under assumed uniform wind conditions. The numerical models allow for the more general conditions of slowly varying wind input and water depths, and can predict the two-dimensional wave energy spectrum. Many uncertainties still remain, but it is clear that a reasonable predictive capability for wind waves presently exists.

Preliminary results of the intercomparison study show substantial differences between some of the models and the measured field data. The reasons for these differences are being examined. Several procedures for entering fetch data are being evaluated. The extra cost, in terms of computation time, of including an algorithm to properly predict wave direction in a strongly varying fetch situation is being evaluated.

PUBLICATIONS

Bishop, C.T. and Donelan, M.A. 1987. Wave prediction models. NWRI Contribution 87-16. In *Coastal Modelling: Techniques and Application,* ed. Laklan, Y.C. and Tranhaile, A.S. Elservier, Amsterdam. In press.

Shore Protection Manual's Wave Prediction Reviewed

C. T. Bishop, Study Leader

M. A. Donelan and K.K. Kahma, (Institute of Marine Research, Helsinki, Findland)

INTRODUCTION

Many engineers use empirical equations with hand-held calculators, nomographs or computer programs to predict wave conditions under an assumed steady-state wind. The two most commonly used sets of equations are those of Sverdrup-Munk-Bretschneider known as the SMB equations, and those of Hasselmann *et al* (1973), known as the JONSWAP equations. A method of applying these equations is provided in the Shore Protection Manual (SPM) of the U.S. Army Coastal Engineering Research Center. The latest version of the SPM, released in 1984, contains several changes in the choice and use of these empirical wave prediction equations compared with earlier SPM editions. This paper examines the impact of these changes using wind and wave data from several sources. The equations of Donelan (1980), which have been favorably compared with JONSWAP and SMB (Bishop 1983), are also used.

RESEARCH RESULTS

The Shore Protection Manual recommends using an adjusted wind speed factor based on friction velocity in the JONSWAP equations for simple steady-state wave predictions. Comparison with measured wave data from various sources reveals that the use of the adjusted wind speed factor leads to overpredictions of wave height and period. Comparison with predictions of the Sverdrup-Munk-Bretschneider (used in 1977 and earlier versions of the SPM), JONSWAP, and Donelan models reveals that the use of the adjusted wind speed factor leads to the poorest statistical results of the four models relative to the measured data. It is suggested that use of the adjusted wind speed factor be discontinued and instead return to using the mean wind speed at a 10 m (33-ft.) elevation.

The use of the JONSWAP relations to replace those of SMB is not recommended based on the comparison with data reported here. The choice of a universal growth curve requires further study, but it is clear that analysis of wave data in terms of wave fetch rather than wind fetch bears serious consideration. We emphasize that the application of computed shear velocity (u_*) values based on empirical wind-dependent drag coefficients, to wave growth curves constructed from mean wind speed directly (or u_* computed using a constant drag coefficient as in JONSWAP) is incorrect and can lead to large errors in estimating waves from wind and fetch information.

PUBLICATIONS

Bishop, C.T., Donelan, M.A. and Kahma, K.K. 1987. Shore protection manual's wave prediction reviewed. NWRI Contribution 86-104.

REFERENCES

Bishop, C.T. 1983. Comparison of manual wave prediction models. ASCE WW 109(1): 1–17.

Donelan, M.A. 1980. Similarity theory applied to the forecasting of wave heights, periods and directions. Proceedings Canadian Coastal Conference, National Research Council of Canada, pp. 47–61.

Hasselmann, K. et al. 1973. Measurements of wind-wave growth and swell decay during the joint North Sea wave project (JONSWAP). Dtsch. Hydrogr. Z., 12:1-95.

Great Lakes Water Levels

C. T. Bishop, Study Leader

INTRODUCTION

High water levels occurred on all the Great Lakes, except Lake Ontario, during 1985-1986, setting new records for the 20th century. Many harbor structures and small craft facilities on the Great Lakes were submerged or overtopped during some storms in this period. Consequently, many cases of structural damage and unacceptably high wave transmission were reported.

Most of the federal harbor structures were constructed between 1900 and 1930. Later reconstructions and additions between 1930 and 1960 continued to use the initial design water levels with some updating. As a result, most of the harbor structures are built to elevations representative of water levels from the period 1900 to 1960, often referred to as the "normal" water levels. This has defined what is accepted as a "normal" elevation for structures and the subsequent freeboard.

Public Works Canada is in the process of developing guidelines for evaluating the need for remedial measures at federal harbor structures and for establishing guidelines for design elevations for new structures. This report addresses historical Great Lakes water level information and looks at possible future levels for the purpose of planning coastal facilities over the next 50 years. In particular, the potential impacts of predicted climate change on Great Lakes levels are reviewed.

RESEARCH RESULTS

A review of available water level measurements since 1815 has provided the ranges for recorded mean monthly water levels as shown in Table 2:

Table 2. Ranges for Recorded Mean Monthly Water Levels (m)

Lake	Max. Monthly Mean	Year	Min. Monthly Mean	Year
Ontario	75.61	1952	73.97	1934
Erie	174.85	1986	173.01	1934-36
			173.0(est.)	1819-21
Michigan-Huron	177.70	1838	175.37	1964
Superior	183.51	1876	182.34	1926
	183.94(est.)	1838		

A plot of annual maximum monthly mean water levels for Lake Erie from 1819 is shown in Figure 6.

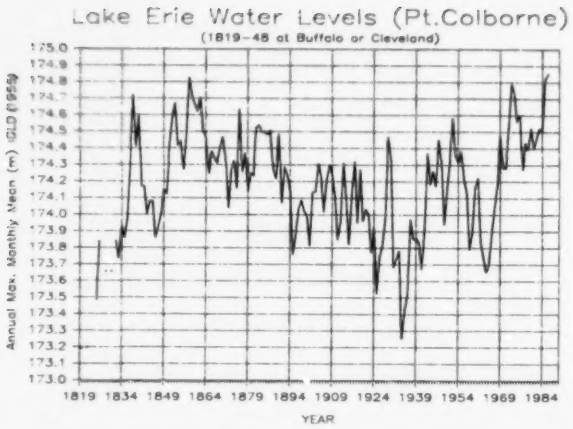


Figure 6. Annual maximum monthly mean water levels for Lake Erie.

There is no direct physical data to suggest that mean monthly Great Lakes water levels have been higher or lower than those given above in the past several hundred years. Future water levels depend mainly on future climate trends. Long-range weather forecasting (in terms of decades) is still in an early developmental stage. Climate appears to be a non-stationary, multi-modal process with evidence of step-function changes. Therefore, statistical analysis of past water level fluctuations in order to provide exceedance probabilities is not valid when there are significant climate changes.

Even if the much heralded greenhouse effect occurs and atmospheric concentrations of CO_2 are doubled, aside from an increase in temperatures, no one can confidently predict climate changes (precipitation, wind, relative humidity, cloudiness, etc.) or the net effect on Great Lakes water levels. On the other hand, if the regional climate continues to be similar to that of the past 150 years, water levels over the next 50 years can be expected to be roughly within the range of those given in Table 2. Simulations with a hydrologic response model indicate that Lake Erie could go as high as 175.0 m IGLD (1955) while Lake Michigan-Huron could go to 177.5 m if a prolonged sequence of abnormally high net basin supplies occurs.

PUBLICATIONS

Bishop, C.T. 1987. Great lakes water levels; a review for coastal engineering design. NWRI Contribution 87-18.

Current Meter Rotor Development

P. Engel, Study Leader

P. Engel

INTRODUCTION

The Price current meter is the instrument used by the Water Survey of Canada (WSC) to measure stream flow velocities. The rotor of the conventional Price meter consists of an assembly of six conical cups oriented symmetrically about a vertical axis of rotation, and is attached to the meter frame. Traditionally, the rotor components have been fabricated out of sheet brass with the whole assembly being protected with chrome or nickel plating. Recently, because of production costs and quality control of this type of rotor, the United States Geological Survey (USGS) has introduced a plastic rotor which can be mass-produced more cheaply, precisely and quickly using plastic injection molds. The WSC wants to adopt a similar strategy and is in the process of developing the necessary mold. Before designing the mold, an attempt was made to modify the geometry of the conical rotor elements of the USGS plastic rotor in the hope of improving the low-speed performance. Such an improvement, if it can be economically incorporated into the mold design, would ensure a better return for the money invested. Three rotor modifications were initially presented, two of which were selected for intensive testing in the towing tank at the National Water Research Institute (NWRI). This study is a joint initiative of WSC and NWRI.

RESEARCH RESULTS

Extensive testing has shown that one of the proposed modifications provides a significant improvement in performance for speeds less than 50 cm/s with threshold speeds of 2 cm/s or less. The design of the rotor lends itself readily to an economical production of a casting mold. Additional tests to determine the effect of reduction of the rotor mass are planned.

PUBLICATIONS

Engel, P., Wiebe, K., De Zeeuw, C. and Terzi, R. 1986. Improvements to the low speed response of the plastic rotor for the Price current meter—Phase II. NWRI Contribution 86-121.

River Flow Measurement Alternatives

P. Engel, Study Leader

INTRODUCTION

Work is under way to explore alternatives to present methods of measuring the discharge of the Milk River at Eastern Crossing, Montana. Accurate discharge data are required at this location to satisfy the water sharing agreement between Canada and the United States as set out by the International Joint Commission. At the present time, streamflow records are not sufficiently accurate because of unstable stage discharge relationships as a result of shifting channel bed and migrating sand waves. Three alternative methods, ultrasonic, electromagnetic, and artificial controls, have been examined. The work was requested by the Water Resources Branch, Calgary, Alberta.

RESEARCH RESULTS

It was found that the ultrasonic method is not suitable for the flow conditions encountered because the flow is very wide and shallow, and sediment concentrations of most flows are too high. The electromagnetic method was found to be unaffected by sediment deposition and technically feasible. If a stable artificial control is to be used, it is important to choose a design which is not affected by sediment movement and deposition. A structure having a flat V-notch crest will increase sensitivity at low flows. Five artificial control designs were selected for detailed evaluation from a large number of available alternatives. The performance of these designs is currently being tested in a physical mobile bed model designed for this purpose with a 1:10 scale ratio. The model with a broad crested weir is shown in Figure 7.

Figure 7. Milk River model.

PUBLICATIONS

Engel, P., Lau, Y.L. and Dick, T.M. 1986. Examination of flow measuring alternatives for Milk River at Eastern Crossing. NWRI Contribution 86-116.

Applied Research and Engineering and National Calibration Service

C. De Zeeuw, Study Leader

J. Marsalek, P. Engel
and staff of the Technical Services Section

C. De Zeeuw

INTRODUCTION

Potential outside users of the Hydraulics Laboratory are encouraged to use the excess capacity on a cost recovery basis. Work taken on in the laboratory ranged from calibration of current meters to construction and testing of hydraulic models. Current meters are calibrated by the National Calibration Service for the Water Survey of Canada and other clients.

RESEARCH RESULTS

The following tables summarize the work undertaken.

Table 3.
Applied Research and Engineering
Fiscal Year 1986/87

Client	Work
Canadian Canners Ltd., Burlington	Analysis of soil samples from a potato-washing machine
Atomic Energy of Canada, Chalk River	Weir calibration
Manitoba Hydro, Winnipeg	Calibration of 30 Ott meters
Morrison Hershfield Ltd., North York	Testing of Avapour barrier
University of Waterloo, Waterloo	Current meter calibration
Ontario Ministry of Environment, Durham	Testing of York-Durham Parshall flume
Monenco Consultants Ltd., Rexdale	Current meter calibration
University of Western Ontario, London	Observing hydroplaning of a towed body
Manitoba Hydro, Winnipeg	Current meter calibrations
Rowen, Williams, Davies & Irwin Inc., Guelph	Tests in cold room using snowmaker
Westinghouse Canada, Hamilton	Testing sonar transducers
Trans-Alberta Utilities, Edmonton	Current meter calibrations
Environmental Management Assoc., Calgary	Current meter calibrations
Acres International, Niagara Falls	Current meter calibrations
McLaren Plansearch, Toronto	Current meter calibrations
Sparton of Canada Ltd., London	Rental of towing tank
University of Manitoba, Winnipeg	Current meter calibrations
Falkenbridge Mines, Falkenbridge	Current meter calibrations
Gov. of Newfoundland and Labrador, St. Johns	Calibrating the Hog-Point flume
Hydro-Québec, Montreal	Evaluation and testing of prototype current meters
Crossman and Swain Inc., Toronto	Testing of catch basin filter

Table 4
National Calibration Service
Fiscal Year 1986/87

Statistics	
Requests received	133
Calibrations performed	887
Hours calibrated	1467
Hours tests performed	385
Calibrations	
622AA Summer Type	429
622AA Winter Type	192
Pygmy Meters	20
Ott Meters	115
Marsh McBirney meters	42
Novar Probes	5
General Oceanic	58
Others	26
TOTAL	887
Clients Served	
Water Survey of Canada	51
NWRI	24
Other federal departments	18
Provincial agencies	15
Hydro companies	7
Consulting engineering	13
Educational institutions	5

List of Agencies Served

Acres International	Niagara Falls
Alberta Agriculture	Lethbridge
Alberta Environment	Edmonton
Alberta Forestry/Lands/Wildlife	Edmonton
B.C. Ministry of Environment	Namaimo
Bedford Institute of Oceanography	Dartmouth
Corey	Ancaster
Dept. of Indian and Northern Affairs	Whitehorse
Dept. of Fisheries and Oceans	Burlington
Dept. of Fisheries and Oceans	Owen Sound
Dept. of Fisheries and Oceans	Quebec City
Dept. of Fisheries and Oceans	Rimouski
Dept. of Fisheries and Oceans	St. Andrews, Nfld.
Dept. of Fisheries and Oceans	St. Johns
Environmental Management Assoc.	Calgary
Environmental Protection Service	Toronto
EPS-Wastewater Technology Centre	Burlington
Falkenbridge	Falkenbridge
Grand River Conservation Auth.	Cambridge
Hydro-Québec	Montreal
Jonathan Nash	Burlington
MacLaren Plansearch Inc.	Toronto
Manitoba Hydro	Winnipeg
Manitoba Natural Resources	Winnipeg
Monenco Consultants	Rexdale
New Brunswick Dept.	Municipal
Affairs and Environment	Fredericton
National Hydrology Research Centre	Saskatoon
NWRI	Burlington
Ontario Environment	Rexdale
Ontario Environment	Thunder Bay
Ontario Environment	Toronto
Ministère de l'environnement du Québec	Ste-Foy
Sparton of Canada	London
The Environmental Applications Group	Willowdale
Trans Alberta Utilities	Calgary
University of Guelph	Guelph
University of Manitoba	Winnipeg
University of Waterloo	Waterloo
University of Western Ontario	London
Water Survey of Canada	All regions
Westinghouse Canada	Hamilton

Research Support Division

J.D. Smith, Chief

J.D. Smith

The Research Support Division is responsible for providing operational scientific support, engineering, and computing services for the National Water Research Institute's research programs, and programs of other on-site agencies at the Canada Centre for Inland Waters. In terms of impact, the ability of the research staff to conduct their programs and the accuracy of their results depend, to a significant degree, on the capabilities and responsiveness of this support infrastructure. The Division, through a centralized support organization, seeks to ensure that the most effective technologies in terms of methods, hardware and personnel capability, are available to support present and future water research and monitoring projects within the NWRI science program. The mandate for the Division encourages support to research at a high level of technical sophistication, while reflecting a commitment to the realities of exercising strict economy in the use of these resources.

Computing and Programming Services provide a complete range of computer, programming, archiving and drafting services. Operational support is provided for systems such as the Great Lakes STAR data base, the LRTAP data base, and the UN Environmental Monitoring Systems (GEMS). Consulting advice on hardware- and software-related subjects, and custom software design and development is provided for the research community. In-house training courses are used to ensure efficient hardware use. Users are kept informed of system changes and developments through the publication of newsletters. A new Control Data Corporation Cyber 830 computer was installed in February 1987. This machine has brought the mainframe computer up to current technology and has significantly expanded the capabilities of the computer facilities for the research community.

The Drafting Office provides drafting, illustrating and photographic support for scientific and technical publications, and visual presentations.

Engineering services provided by the Division include the design, manufacture and calibration of a complete range of scientific sampling and measurement equipment for use in the various Institute studies and those of other client organizations. In addition, this section provides NWRI's liaison and contract management for Environment Canada's program for industry/laboratory projects (PILP). The contribution to the Institute's science progam includes a broad range of engineering and technical services including a consultation role. As part of their mandate, the associated engineers and technologists must anticipate requirements for new equipment and systems in order for the Institute to remain at the forefront of instrument design and development in the various limnological fields. For in-house engineering projects, close cooperation and coordination is maintained between the client and the design and manufacturing phases in order to produce state-of-the-art instrumentation, most of which is used in hostile environments and where instrument failure has severe consequences on scientific program delivery.

During 1986/87, a wide range of items were manufactured by the Engineering Section including a clam dredge, a groundwater bore-hole straddle packer, a compaction mold and a volume-weighted sampler. Two large-scale projects were undertaken. The WAVES (Water Air Velocity Experiment), year two of a three-year program, set out a large array of air-water interface instrumentation at the offshore NWRI Research Platform. High frequency wind-wave and associated measurements from over 100 sensors were monitored. For the UGLCC (Upper Great Lakes Connecting Channels), a high capacity data logging system was developed. Other projects included the evaluation of a multi-parameter logger, the expansion of the capability of the Dissolved Oxygen Profiler to include conductivity, and its extensive use in the Hamilton Harbour Project. In terms of systems development, progress on the cytometer system generated sufficient enthusiasm within the science community at NWRI to carry the development through a prototype stage during the upcoming fiscal year.

The third service provided by the Division is technical operations, presently organized as two sections, one pro-

viding shore-based field operations, the other providing ship operations support. These sections work closely to support NWRI water research and surveillance programs such as LRTAP and the GLWQA. Other clients include Fisheries and Oceans, the National Water Quality Laboratory, the Ontario Ministry of the Environment, various Environment Canada agencies and local universities. The activities of these sections range from the planning and operation of field laboratory sites, equipment, facilities, rigging, diving operations and data and sample collection from launches and aircraft, to the coordination and conduct of multidisciplinary scientific cruises aboard major research ships.

During 1986, Technical Operations provided training to staff at the University of Alberta on techniques for application of lime for lake restoration. Scientific staff of the Quebec Ministry of the Environment were trained in the operation of the Lightweight Corer Sediment Sampling device. Field monitoring and surveillance support was provided to the Ontario Ministry of Natural Resources.

A new technique for water sampling aboard the CSS *LIMNOS* was developed for operations on the St. Lawrence River.

Science Liaison Division

R.J. Daley, Chief

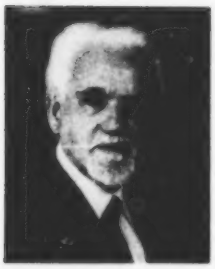
R.J. Daley

The Science Liaison Division provides an institutional focus for managerial coordination of NWRI's annual research program, the strategic research planning process and corporate policy development and communications. The Division also controls and conducts the Institute's general communications and information program which encompasses media relations, program marketing, coordination of research publications, interaction with the international water science community, and library services for NWRI and other components of the Canada Centre for Inland Waters.

Included within the Division are the senior scientist of NWRI, the senior research management advisor, and the manager of the World Health Organization's global Collaborating Centre on Surface and Groundwater Quality, all of whom, in addition to their advisory or managerial responsibilities, conduct their own research studies.

Elemental and Biochemical Composition of Plankton Biomass

R.A. Vollenweider, Study Leader



R.A. Vollenweider

The following is an excerpt from the publication:

Vollenweider, R.A. 1985. Elemental and biochemical composition of plankton biomass; some comments and explorations. Arch. Hydrobiol. 105(1): 11-29.

This passage expresses the theme which has been taken up in much greater detail over 1986-87. This research has important implications for management of the productivity of the Great Lakes and other water bodies.

Contrary to the present tendency to consider the C:N:P ratio in plankton as a kind of structural normative, we have given more emphasis to derivation of the elemental composition of biomass from its main biochemical characteristics. While the Redfield ratio may represent a valid summary expression for the integrative biogeochemical processes in open marine waters, in freshwaters (as well as in many coastal marine waters), the C/P and the N/P ratios in plankton range from ratios of half to twice and three times the Redfield ratio (Vollenweider & Harris, in prep.). Variations in these ratios reflect fundamental shifts in the relative proportions of the main biochemical compartments (proteins, carbohydrates, lipids) which from a tropho-dynamic point of view are more meaningful than the ratios per se. Variations in the biochemical make-up of freshwater plankton, as related to the nutritional environment, has been well documented (for review Healy 1975), while Goldman *et al.* (1979) have drawn attention to the relationship between elemental ratios and growth rates in marine waters.

Shifts in the protein/carbohydrate/lipid ratios give rise to changes in the C/N ratio which can be due either to phosphorus or nitrogen limitation. Therefore, the C/N ratio is not only indicative of the characteristics of the milieu in which a given biomass has been produced, but the C/N ratio lends itself for a crude interpretation of the relative proportions of proteins/non-proteins in plankton biomass.

Nonetheless, the assumption that all nitrogen is in protein, and that protein can be calculated from nitrogen by a simple conversion factor (commonly assumed to 6.25) is open to question. In zooplankton, if chitin is present, this is definitely not the case. In phytoplankton, the problem is not clear either. Di Tullio *et al.* assume 85% of the total nitrogen pool to be in protein (which would give a conversion factor of only 5.3), while Parsons *et al.* have found that the ratio between colorimetrically determined proteins (nitrogen x 6.25), on average, is about 1.3. In other words, 6.25 would give an underestimate. Such uncertainty, of course, sets limits to the interpretability of the C/N ratio in terms of protein/non-protein.

In order to make the Spoehr & Milner approach more reliable, not only this question has to be clarified, but also the question of what indeed are the prevailing elemental and biochemical compositions of plankton biomass, and their variability, under varied environmental conditions. The most uncertainty at the present time is in regard to the proportions of hydrogen and oxygen in biomass. It has been shown that the proportions assumed by Stumm & Morgan (1970) are unrealistic as a general rule, particularly in regard to oxygen, while hydrogen may vary more widely. However, the difficulty with hydrogen is the fact that in terms of percent composition the variations are modest. Nonetheless, such variations are highly significant when considered in the light of their relationship to the biochemical make-up. This is clearly evidenced by the analysis of the *Daphnia hyalina* life cycle, as well as the *Chlorella* example, both of which indicate that knowledge of the hydrogen fraction can lead to, at least in principle, meaningful additional characterization of biomass properties. The approach taken in this note to the energy question, on the other hand, is admittedly crude. Nevertheless, the examples show sufficiently clearly that a broadening in scope of approach is needed. Though the problem is complex, it would be desirable to pursue this matter with the rigor of the theoretical chemist. Equations of formation and mineralization should not only be plausible, but also energetically defendable. While this may not be possible in the near future, intermediate aspects, such as the degree of reduction (Spoehr & Milner), or the oxidation state concept

(Stumm & Morgan), could be taken up in the interim, and related to production dynamics.

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Goldmann, J.C., McCarthy, J.J. and Peavey, D.G. 1979. Growth rate influence on the chemical composition of phytoplankton in oceanic water. Nature 279, 5710: 210–215.

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Spoehr, H.A. and Milner, H.W. 1949. The chemical composition of *Chlorella;* effect of environmental conditions. Plant Physiol. 24: 120–149.

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Phosphorus Relative Residence Time: An Approach to Understanding Sedimentation and the Trophic Response of Lakes

Lorraine L. Janus, Study Leader

R.A. Vollenweider

L.L. Janus

CONTEXT AND PROBLEM

The objective of the research carried out in 1986/87, in a general context, is to understand the complexes that control aquatic productivity in order that water quality can be preserved or controlled. An understanding of production-controlling complexes, or more specifically nutrient fluxes, will ultimately lead to refinements in predictions of biological response and ultimately revision of management criteria such as critical nutrient loads. Biological production is not only important in and of itself as a factor which directly modifies water quality, but also because of its role in regulating the chemical composition of surface waters, via its metabolism and surface chemistry, including its role in contaminant removal.

The prediction of biological response to the contamination of surface waters with growth-promoting substances is a complex (i.e., multifaceted) problem. Not only are the concentrations, chemical availability, and exposure of nutrients modified by the physical, chemical, and biological characteristics of each lake basin, but the final result (i.e., productivity level) varies according to the slowest phase (i.e., "bottleneck") of nutrient cycles. Therefore each basin assimilates its nutrient load in a different way.

APPROACHES

Historically, the prediction of lake production has evolved from being based on nutrient concentration (a static measure), to supply rate (a dynamic measure of input), to the present development of residence time (a dynamic measure of the balance between supply and elimination). Nutrient residence times are defined as a quantity divided by its replacement rate, and describe the time period during which a given substance remains within the water column. Residence times are determined by the general processes of hydraulic flushing and sedimentation, each of which varies in efficiency according to physical, chemical, and biological factors. If residence times for phosphorus — the main production controlling factor — are calculated relative to water flows, the resulting "relative residence time" (τ_p/τ_w), is determined primarily by sedimentation. Since sedimentation is the least understood aspect in the prediction of nutrient effects, relative residence times offer a means for its quantitation and functional analysis.

We have been approaching the analysis of relative residence time of phosphorus from two directions: the analysis of cross-sectional data for many lakes with only one year of data, and time-series studies on individual lakes with consecutive years of data. The two are complementary and neither is optional. Variation on the large spatial scales of cross-sectional data relates to geological and morphometric features. The data base which we have compiled for such analysis represents approximately 20% of the earth's supply of fresh water, and as such is sufficient to provide a representative sample. This data confirms the earlier contentions of R.A. Vollenweider that phosphorus residence time on the grand scale is controlled by flushing rate and that water residence time is a good general estimate of sedimentation. A further discovery from this data set was that (τ_p/τ_w) vs. P_i (Fig. 1) is characteristic of

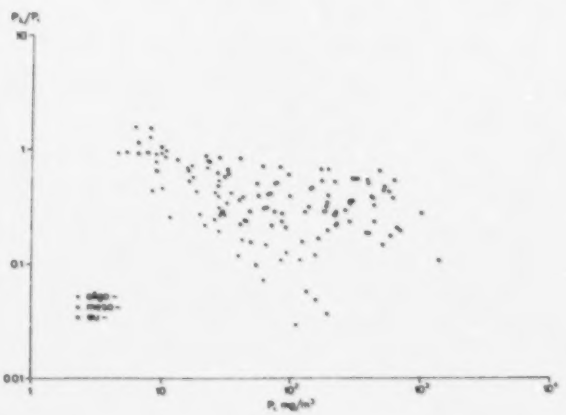


Figure 1. Phosphorus relative residence time vs. phosphorus inflow concentration.

different trophic states. In essence, it indicates that net sedimentation is lower in eutrophic lakes than in oligotrophic lakes. We are presently working to analyze the reasons for this phenomenon with the complementary temporal series.

We have also been compiling the data on long-term case studies. This will allow us to separate the functional from the coincidental relationships found in cross-sectional data and to pinpoint the primary controlling factors for sedimentation in individual basins. Despite the fact that few consistent long-term nutrient budgets for lakes exist, we have been able to identify lakes in which water residence time cannot be used to estimate sedimentation. Other relationships will have to be formulated to describe these cases. Furthermore, the long-term evolution to sediment saturation (and subsequent loss of absorptive capacity) with long-term enrichment pressures, and the fact that short-term processes may override the long-term effects, has become clear from our investigations.

IMPLICATIONS

The implications of our work are that nutrient loading criteria and response rate calculations must take into consideration the past history and present trophic condition of a lake, and this can be evaluated through a study of the behavior of phosphorus residence times. With the qualitative knowledge of sedimentation relationships which we have gained in the past year, we have established the direction for future quantitative studies to improve our capabilities of predicting biological production in lakes.

Development of Thermal Structure in Lake Ontario

G.K. Rodgers, Study Leader

G.K. Rodgers

INTRODUCTION

Earlier studies, based on less than 5 years of data, indicated the potential for developing a relation between winter temperatures and the time at which thermal structure was complete across the lake. Now with 22 years of record, this earlier indication has been borne out. This relation allows a reasonable predictive capability for the timing of these events and the general nature of the thermal structure that will develop.

RESEARCH RESULTS

The relation between the mean temperature of Lake Ontario (mid-lake to 100 m depths) in April and the date of onset of complete thermal structure across the lake (the date of disappearance of the thermal bar) is shown in Figure 2. There is also a reasonable correlation between the April water temperature and the mean air temperature of the previous four winter months (Fig. 3).

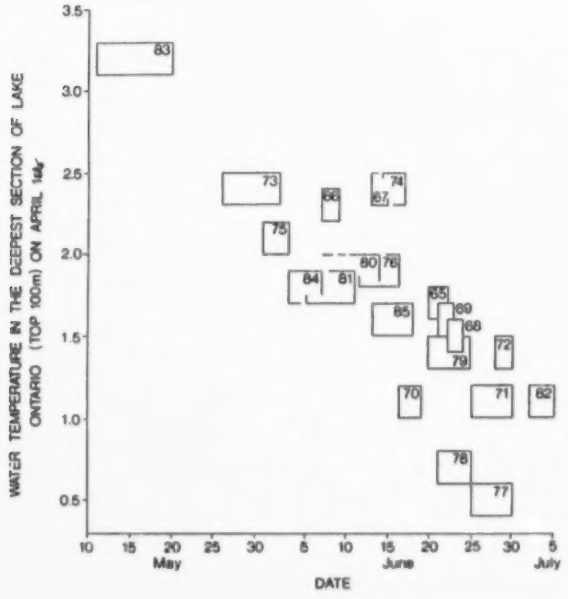


Figure 2. Date of full stratification or disappearance of the surface 4°C isotherm as function of April 1st water temperature. (Deep region east of 77° 45'W longitude in Lake Ontario.)

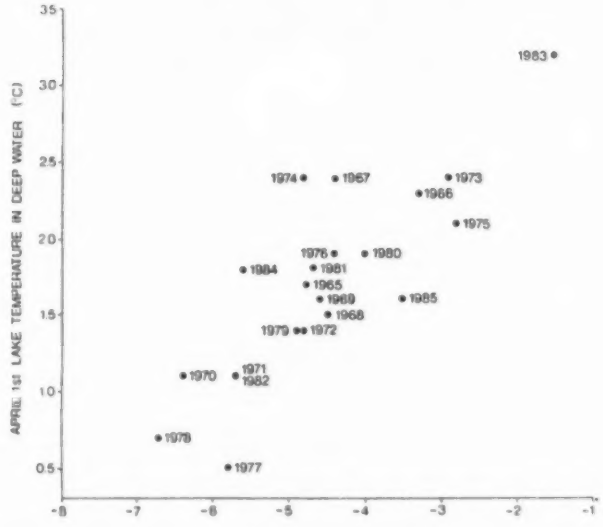


Figure 3. Mean air temperature at Pearson Airport — preceding Dec. - Mar. (°C).

Elaboration of this situation in relation to the consequences of the unusually warm "El Nino" weather (winter 1982/83) has prompted interest in its impact on the distribution of fish in the lake in spring, and in the incidence of taste and odor events at water intakes along the northwest shoreline of the lake.

PUBLICATIONS

Rodgers, G.K. 1987. The time of onset of full thermal stratification in Lake Ontario in relation to lake temperatures in winter. NWRI Contribution 87-117. Can. J. Fish. Aquat. Sci. In press.

WHO Collaborating Centre on Surface and Groundwater Quality (WHO/CC)

S. Barabas, Study Leader

S. Barabas

INTRODUCTION

Established in October 1974 by an agreement between the World Health Organization and the Department of the Environment, WHO/CC is engaged in the following major activities: (1) global coordination of the GEMS/Water project, (2) publication of the quarterly journal *Water Quality Bulletin* in separate English and French editions, and (3) coordination of technical assistance programs to developing countries.

The following is a brief review of the first two activities.

GLOBAL ENVIRONMENTAL MONITORING SYSTEM FOR WATER (GEMS/WATER)

This is an ongoing United Nations project mandated at the United Nations Conference on the Human Environment held in Stockholm, Sweden, in June 1972. The specific objectives of the GEMS/Water project can be summarized as follows: (1) monitoring the incidence and long-term trends of pollutants in water; (2) assisting the participating countries who so desire in establishing their own national monitoring network; (3) improving the validity and comparability of water quality data within and between the participating countries; (4) providing advance warning of any serious deterioration; and (5) prompting governments to initiate, individually or collectively, corrective action for the protection, restoration, and improvement of the environment.

The project was put into effect in 1977, and the collection of water quality data started in January 1979. As of January 1987, water quality data from about 450 monitoring sites on major rivers, lakes and aquifers in 60 countries were being reported to WHO/CC at NWRI. The variables monitored fall into two categories: (1) basic variables (from temperature, pH, and electrical conductivity to dissolved oxygen, nitrates, nitrites, sulfates, phosphates, and chlorophyll; and (2) use-related variables, comprising those of interest for drinking water supplies, agriculture, and aquatic life.

Recent evaluation of water quality data by water body (rivers, lakes, and aquifers) shows the following:

Rivers

The drainage area covered by each monitoring station varies from as little as $10 km^2$ to over $2 \times 10^6 km^2$ as for the Mississipi, Nile, Parana, and Yang Tse Kiang rivers.

Monitoring is generally satisfactory for the basic variables, and less so for heavy metals, organochlorinated compounds, and nutrients.

Faecal Coliforms

Very disturbingly, high levels of faecal coliforms were detected on all continents. They are common in many rivers of India, Pakistan, Indonesia (up to 10^6/100 mL) and Mexico, and to a lesser degree in Spain, the United States, the United Kingdom, and in the river Rhine (of particular concern as it is an international body of water). Assessment of faecal contamination in many rivers was not possible for lack of data (particularly in Africa).

BOD, COD, DO, and Nutrients

Evidence is found everywhere of major urban pollution of rivers from high levels of BOD_5, COD, and nutrients resulting in low DO values. Based on the available data, such pollution is particularly significant in Ecuador, Guatemala, India, Malaysia, Mexico, Turkey, and the United Kingdom. This does not include countries that did not report such data. Of particular significance is the pollution of the Tzepala River in Guatemala, which was selected as a baseline station, i.e., considered unaffected by human activities. A reclassification of the monitoring site on this river into an "impact" station is justified.

Heavy Metals

Metal concentrations in excess of 20 times the natural levels in rivers were taken as indicators of pollution. High levels were found in the rivers of Chile, China, Japan, Mexico, Panama, the Philippines, Turkey, and the United States (Rio Grande). In many instances, the high metal concentration was difficult to explain unless the samples were not filtered from suspended matter. In Rio Mapocho (Chile), classified as a baseline station, high copper values were found, which call for reconfirmation and, if reconfirmed, for an indication of the source of copper contamination.

Pesticides

Regrettably, many countries lack the instrumentation necessary for monitoring pesticides. The available data show evidence of pesticide contamination in China, New Zealand, and the Philippines.

Problems with Natural Water Quality

The data show that in many countries the natural water quality of rivers may be unfit for many uses. Among the problems encountered are the following:

(1) High suspended solids were found in a number of mountainous countries such as China, India, Indonesia, the Islamic Republic of Iran, Pakistan, and Turkey; they cause problems in water treatment.

(2) High dissolved solids (salinity, Na^+, Cl^-, and $SO_4^=$) exceeding the values found in the WHO guidelines were encountered in some of the rivers in Australia, northwestern India, the Islamic Republic of Iran, and Mexico.

(3) High fluoride levels were found in rivers of volcanic and arid regions. Severe health problems from such causes were reported from the United Republic of Tanzania with respect to the Rifiji and Kagera rivers. High fluoride levels were also reported from the Nile delta area and in Mexican rivers (Colorado, Conchos, Bravo, Cotzacoalcos, and Balses). Continued monitoring of such rivers is essential.

Lakes

Coverage

The lake network comprises 66 lakes approximating 30 000 km^3 or about 30% of all freshwater resources stored in lakes (Caspian Sea excluded). However, most stations were located at the lake outlets, which is inadequate for fully assessing lake water quality. If the lake coverage were to be considered on the basis of stations located at the lake centers, where sampling is carried out at multiple depths, the GEMS/Water lake coverage would drop to 12.6% of the total world lake area, or about 8.5% of the total lake volume.

All reservoirs monitored, with the exception of Lake Nasser on the river Nile, are small; they are mostly city water intakes. Regrettably, the world's largest reservoirs, such as Kariba on the Zambezi river (volume 156 km^3, area 5364 km^2), Volta on the Volta River (volume 165 km^3, area 8845 km^2), and many others found in the Soviet Union are not included in the GEMS/Water program.

General Assessment

The analytical data available were inadequate for drawing significant conclusions. Serious drawbacks were noted in all aspects of lake water monitoring ranging from sampling procedures and frequency of sampling to the selection of analytical variables and data coding.

Such observations have led to redefining the objectives of lake monitoring to include the following four major human health and environmental concerns: eutrophication, acidification, metal and organic pollution, and microbiological pollution.

Monitoring for eutrophication will require sampling along appropriate depth profiles depending on lake depth; and for horizontal coverage of the lake, there should be one station per selected unit area, the number of stations being increased in proportion to the logarithmic increase in lake area.

Important lake data such as chlorophyll, transparency, and algal composition should be added to the data base.

Likewise, monitoring of lake sediments should be initiated as they are indicative of long-term trends of pollution, whether of natural or anthropogenic origin.

Groundwaters

General Assessment

Although 19.2% of all monitoring sites are for groundwater monitoring, only 6.2% of the GEMS water quality data relate to groundwater.

The following observations can be made with respect to groundwater quality:

1. Two-thirds of the monitoring stations show some faecal pollution.

2. Many of the same stations show high BOD and N values.

3. Fewer than one-fifth of the groundwater stations report the globally significant variables. Lead and fluoride were above the WHO guideline values for drinking-water quality in only two cases. High values for arsenic, nitrates, manganese, iron, and phenol were found in one case for each element.

4. The available data did not indicate any seawater intrusion or pesticide contamination.

CONCLUSIONS

Although the period under review in the implementation of this ambitious project is too short to allow any conclusions to be drawn with respect to the long-term incidence and trends in water pollution, and the quarter of a million data points reported so far from some 450 monitoring sites in 60 countries represent but a fraction of the data needed for meaningful interpretation, a beginning has been made. And that may have been the most difficult part of the whole project.

Considering that 60 countries, of varying cultural, social, and economic backgrounds, are motivated to join in an international cooperative effort that directly or indirectly reflects their very lives is an accomplishment in itself. Monitoring of natural water and evaluation of trends is essential to the preservation of water quality, which is fundamental in the maintenance of an adequate and safe water supply, necessary for good health.

More than half of the countries participating in the GEMS/Water project have never had their own national water quality monitoring program. Now they have been stimulated to start one. The data they report undergo an international review in terms of both analytical validity of data through the analytical quality control program and data interpretation by an international panel of experts.

By designating a center or a laboratory as the national focal point for the GEMS/Water program, each country is laying the foundations for the establishment or future expansion of its own national water quality monitoring network. These national centers will eventually serve as training centers for chemists and technicians in other laboratories in the country and ultimately initiate and lead a national interlaboratory quality assurance program. This is particularly important for those developing countries which may not have been in a position to carry out water quality monitoring before.

WATER QUALITY BULLETIN

The April 1986 issue of the *Bulletin* was devoted to reviews of water management practices in Australia, Indonesia, Malawi, Senegal, Thailand, Toto, and Tunisia. One article dealt with eutrophication modelling for water quality and another with approaches to community participation in developing countries.

The July and October 1986 issues of the *Bulletin* were devoted to the theme of Acid Precipitation and Human Health. In all, 20 articles were published by authors from Canada, Denmark, Hungary, Norway, Poland, Sweden, the United Kingdom, the United States and Yugoslavia. A full gamut of concerns pertaining to the impact of acid rain on groundwater, streams, lakes, and ultimately drinking water and its effect on human health was covered.

The January 1987 issue of the *Bulletin* was devoted to the theme of Water for Agriculture. It was prepared in close cooperation with the United Nations Food and Agriculture Organization (FAO) and it contained eight articles written by authors from Egypt, Hungary, India, the United Kingdom, and the United States. This was the first of two issues scheduled on this theme. The concerns pertaining to the effects of water quality on land, crops, crop yield, food, and ultimately human health were amply treated.

PUBLICATIONS

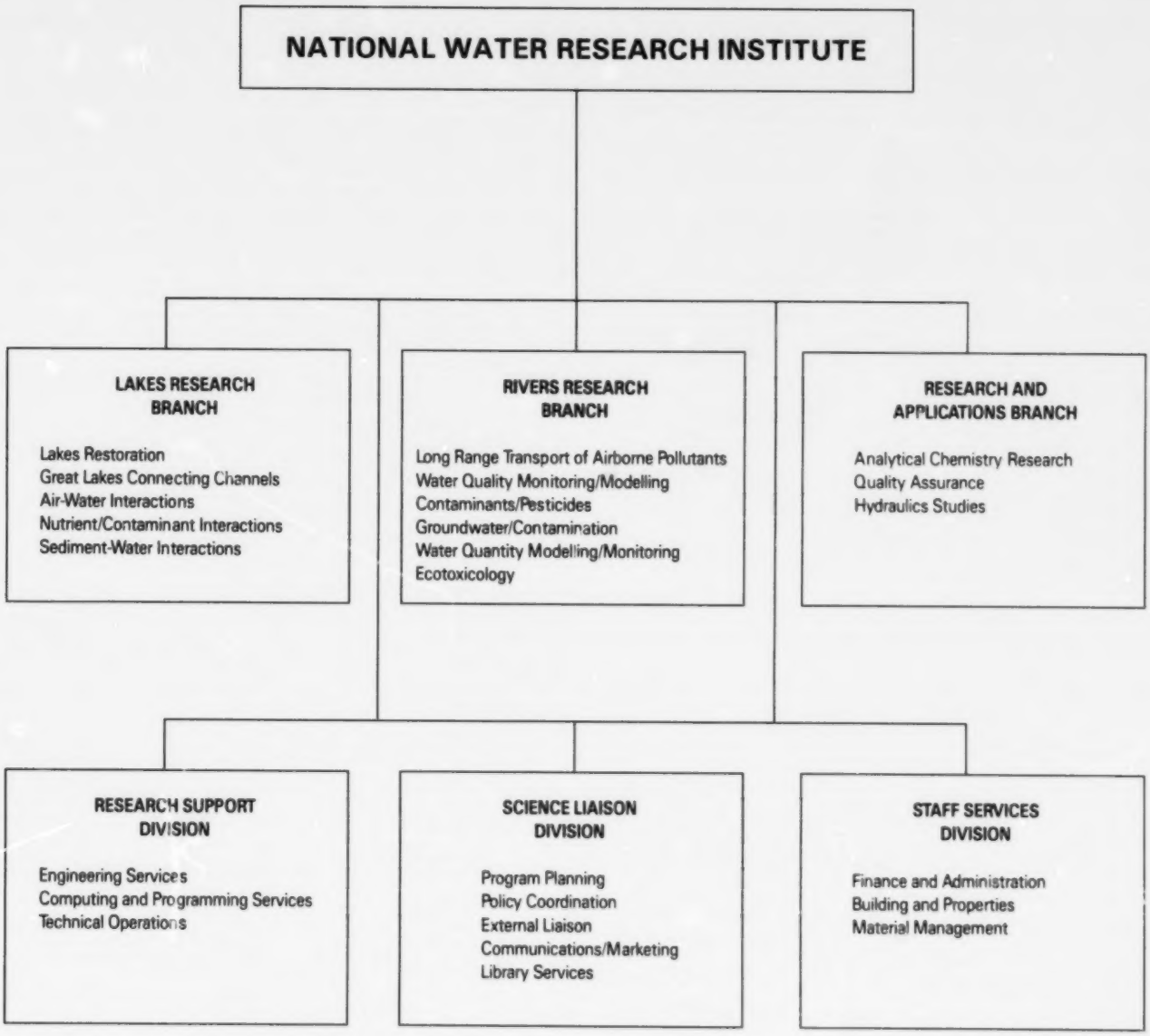
Barabas, S. 1986. GEMS/Water - A United Nations Program for Global Water Quality Monitoring. Invited lecture given at the International Symposium on Natural Environment Monitoring, Jablona, Poland, December 1986, 12 p.

Barabas, S. 1986. Monitoring natural waters for drinking-water quality. World Health Statistics 39(1): 32–45.

Barabas, S. 1986. Surveillance de la qualité des eaux naturelles destinées à la consommation. Rapp. trimest. statist. mond. 39(1): 32–45.

APPENDICES

Appendix A Organization Chart



ERRATA

Due to an editing error the degree abbreviations listed in the next section incorrectly follow the system of nomenclature used in the United States of America. For those degrees obtained at institutions **NOT** located in the U.S.A., the correct designations are:

B.Sc.	instead of B.S.
B.A.Sc.	instead of B.A.S.
B.Eng.	instead of B.E.
M.Sc.	instead of M.S.
M.A.Sc.	instead of M.A.S.
D.Sc.	instead of D.S.

Appendix B
Staff List

NATIONAL WATER RESEARCH INSTITUTE

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AND RESEARCH SPECIALTIES

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CHIEF, RESEARCH SUPPORT DIVISION

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environmental toxicity of yeast and fungi

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J.A. Kraft
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Appendix C
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- IJC Science Advisory Board
- Vice-President, Canadian Association for Water Pollution Research and Control (IAWPRC)
- Chairman, Canadian Great Lakes Water Quality Agreement - Toxic Chemicals Committee

Barica, J.M.
- IJC Eutrophication Issue Group of Great Lakes Water Quality Work Group

Boyce, F.M.
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- Advisory Board to the Great Lakes Program, State University of New York (Buffalo)

Burnison, B.K.
- Associate Member, Faculty of Graduate Studies, University of Guelph

Carey, J.H.
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Charlton, M.N.
- IJC Surveillance Work Group
- COA Surveillance Subcommittee
- IAGLR Board of Directors
- IJC Lake Superior Task Force

Coakley, J.P.
- IJC Water Quality Board Sediment Subcommittee
- IUGS Committee on Sedimentology
- Hamilton Region Conservation Authority Water Management Advisory Board

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- IJC Lake Superior Task Force

Glooschenko, W.A.
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- DOE Coal Committee
- Canadian representative Society of Wetland Scientists

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Hamblin, P.F.
- Scientific Committee, Canadian Meteorological and Oceanographic Society
- Membership Committee IAGLR

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- DOE Nuclear Advisory Committee
- ISO Water Quality/Radiological Methods Subcommittee
- Canadian Uranium Producers' Metallurgical/Analytical Subcommittee

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- Upper Great Lakes Connecting Channels Work Group

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- IJC Water Quality Board, Sediment Subcommittee
- MISA 5th Working Group
- Bioassay Working Groups, U.S. Army Corps of Engineers

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- Thesis Committee M.S., University of Alberta

Nagy, E.
- MacKenzie River Contaminants Advisory Group

Painter, S.
- Board Member, Aquatic Plant Management Society

Reynoldson, T.
- Cochairman, Upper Great Lakes Connecting Channels Task Force, IJC
- IJC Water Quality Board Sediment Subcommittee
- Science Advisory Board, Mesotrophic Work Group

Rosa, F.
- IJC Lake Erie Task Force

Schertzer, W.M.
- IWD Hydrological Research Program Committee

Sly, P.G.
- Remedial Action Plan, Bay of Quinte
- Great Lakes Fishery Commission, Lake Ontario Habitat Advisory Committee
- Cochairman GLFC/IJC Committee on Classification and Inventory of Great Lakes Aquatic Habitat
- Oil and Gas Lands Administration, Offshore Structures Foundations Committee

Strachan, W.M.J.
- Chairman, IJC Science Advisory Board's Aquatic Ecosystems Objective Committee
- DOE-NH&W Toxic Chemicals Committee
- DOE Great Lakes Water Quality Program Toxic Chemicals Committee
- Chairman, IJC Coordinating Committee for the Assessment of Chemicals in the Great Lakes Ecosystem
- IJC Water Quality Board's Atmospheric Deposition Monitoring Task Force
- IJC Science Advisory Board's Modelling Task Force

Zeman, A.J.
- Chairman, Symposium on Cohesive Shores

RIVERS RESEARCH BRANCH

Beltaos, S.
- Chairman, NRCC (National Research Council of Canada) Working Group on River Ice Jams
- NRCC Subcommittee on Hydraulics of Ice Covered Rivers
- NRCC Task Force on Numerical Modelling of River Ice Conditions
- IAHR (International Association for Hydraulic Research) Working Group on River Ice Hydraulics
- New Brunswick Subcommittee on River Ice
- Chairman, Technical Program Committee, NRCC Workshop on River Ice Jams, Winnipeg, 1986
- Chairman, Ice Jams and Flooding Seminar, 23rd Congress of IAHR, Ottawa, 1989

Bobba, A.G.
- President, Ontario Section, American Institute of Hydrology
- Inland Waters Directorate Hydrological Research Program Committee

Bourbonniere, R.A.
- Peat Environmental Committee (DOE-Provinces)
- Kejimkujik Calibrated Catchments Working Group
- CCIW Library Committee

Chau, Y.K.
- Ph.D. Committee, Geology Department, McMaster University
- Professor (part-time), Department of Geology, McMaster University (Supervisory Committee)

Day, K.E.
- Co-organizer, 1989 SETAC meeting, Toronto, Canada

Dutka, B.J.
- ASTM (American Society for Testing and Materials)
- ISO (International Standards Organization)
  - Canadian Chairman, Subcommittee SC4 (Microbiology)
  - International Secretariat - ISOTC147/SC4/WG9 (Membrane Filters)
- APHA (American Public Health Association) Consultant to and Task Group Member for revision of APHA Standard Methods
- AWWA (American Water Works Association), Microbiological Problems Committee
- WHO (World Health Organization), working member of panel to update WHO Manual on Analysis for Water Pollution Control
- National Aquatic Biomonitoring Committee
- Municipal and Industrial Strategy for Abatement Program
- Cochairman, Toxicity Testing Symposium Committee
- Cochairman, Water Quality Symposium Committee

El-Shaarawi, A.H.
- Chairman, Data Interpretation Group for Niagara River. [A group of representatives from Environment Canada (DOE), Ontario Ministry of the Environment (MOE), New York State and Environmental Protection Agency (EPA)
- Graduate Committees on Statistics at McMaster and Western Ontario universities
- Elected Member, International Statistical Institute

Jackson, R.E.
- Upper Great Lakes Connecting Channels Working Group on Non-Point Sources
- DOE/MOE Chemical Valley Hydrogeology Working Group
- Transport Canada's Gloucester Landfill Technical Committee

- Great Lakes Toxic Chemical Committee, Federal Government
- CCREM Waste Disposal Site Monitoring Methodologies Working Group.

Jeffries, D.S.
- Turkey Lakes Watershed Steering Committee
- LRTAP Research and Monitoring Coordinating Committee, Quality Assurance Subgroup

Krishnappan, B.G.
- Technical Committee-Water Quality and Quantity Committee of Flathead River International Study Board, IJC
- Chairman, CSCE Task Force on River Models.

Lam, D.C.L.
- IAEA (Internationial Atomic Energy Agency) Working Group on Coastal Modelling
- IAWPRC (International Association of Water Pollution Research and Control) Specialist Technical Group on Systems Analysis in Water Quality Management
- LRTAP National Assessment Task Force, Aquatic Effects
- Ph.D. Candidate Supervisory Committee, Department of Civil Engineering, McMaster University

Lau, Y.L.
- CSCE (Canadian Society for Civil Engineering) Hydrotechnical Division Research Committee
- Organizing Committee, Symposium on Interbasin Transfer of Water
- Ph.D. Supervisory Committee, Department of Civil Engineering, Queen's University
- Executive Committee, IAHR (International Association for Hydraulic Research) Congress, 1989

Liu, D.L.S.
- Associate Professor of Environmental Toxicology, Tulane University School of Public Health and Tropical Medicine, New Orleans, U.S.A.
- Registry of Experts in Aquatic Sciences and Marine Pollution, FAO, Rome, United Nations
- Consultant, PEPAS/WHO/UN on Water Quality and Environmental Health Monitoring (PEPAS-promotion of environmental planning and applied studies)
- Canadian Chairman on Biodegradability, ISO/TS 147 WG4
- Consultant, Wastewater Technology Centre, Burlington, Ontario
- Regional Secretary for Eastern Canada, International Biodeterioration Society
- Society for Environmental Geochemistry and Health
- Co-organizer, Third International Symposium on Toxicity Testing Using Microbial Systems, May 11-15, 1987, Valencia, Spain

Maguire, R.J.
- DOE-NH&W Environmental Contaminants Act 4(6) Chemical Evaluation Committee
- Committee for Environmental Monitoring of Forest Insect Control Operations (DOE-New Brunswick MNR)

Marsalek, J.
- Technical Committee for the Waterford River Basin Study (Federal-Provincial Committee)
- Urban Water Resources Research Council, ASCE
- Task Committee, U.S. Geological Survey on Gauging Networks in Urban Areas
- UNESCO Working Group on Urban Hydrology
- Co-rapporteur for the International Hydrological Programme III, Project on Management of Urban Water Resources

Novakowski, K.S.
- Niagara River Toxics Management Plan, Non-Point Source Subcommittee

Nriagu, J.O.
- Canadian National Committee for SCOPE
- SCOPE Scientific Committee on Metal Cycles
- International Committee for Symposia on Environmental Biogeochemistry
- IAGC (Internat. Assoc. Geochem. Cosmochan.), Working Group on Geochemistry and Health and Disease

Ongley, E.D.
- Canadian Committee for SCOPE
- Secretary-Treasurer, International Association for Sediment-Water Science
- Consultant, Pan American Health Organization
- Great Lakes Working Group: Eutrophication Issues Committee
- Environment Canada Pesticides Program Management Committee
- Consultant, U.S. Geological Survey, Quality of Water Division
- Consultant, U.S. Geological Survey, Water Resources Division
- Professor (part-time), Department of Geography, McMaster University (Supervisory Committee)
- Water Resources Branch, DOE, Sediment Survey Task Force

Rao, S.S.
- Lake Huron Task Force
- Chairman, ASTM Subcommittees on Water
- Associate Member, Graduate Advisory Committee (M.S.) - Brock University, St. Catharines, Ontario; University of Toronto, Toronto

RESEARCH AND APPLICATIONS BRANCH

Aspila, K.I.
- Chairman IJC Data Quality Work Group
- IJC Surveillance Work Group
- LRTAP Quality Assurance Subgroup
- LRTAP Terrestrial Intercomparison Work Group
- UGLCCS Quality Management Work Group

Bishop, C.T.
- Great Lakes Hazard Lands Technical Committee

Chau, A.S.Y.
- AOAC Quality Assurance Committee
- Coordinator for Water and Sediment FICP Check Sample Program
- Chairman, Quality Management Work Group, Upper Great Lakes Connecting Channels Study
- Research Board of Advisors, National Division, American Biographic Institute

Cheam, V.F.
- American Chemical Society (Division of Environmental Chemistry)

Donelan, M.A.
- Model Function Committee of NASA-NSCAT Scatterometer Project
- Working Group 83 (Wave Modelling) of SCOR - Scientific Committee on Oceanic Research
- Working Group on Air/Sea Fluxes of the Joint Scientific Committee of the World Climate Research Programme and the Committee on Climatic Changes and the Ocean
- European Wave Modelling Group (WAM)
- NASA-NSCAT (Navy Scatterometer) Science Definition Team
- American Meteorological Society Committee on the Interaction of the Sea and Atmosphere
- Science Committee, Canadian Meteorological and Oceanographic Society
- Canadian National Committee for SCOR

Goulden, P.
- CCIW Library Committee
- NWRI representative in IWD Technical Training Committee

Lee, H.B.
- Associate Referee for Herbicides, Committee H, Water Methodology, AOAC
- Associate Referee for Organo-phosphate, Committee G, Organo-phosphate, AOAC
- AOAC

Scott, B.F.
- Department of Environment Emergency Team (DEET Ontario)

EXECUTIVE DIRECTOR AND SCIENCE LIAISON DIVISION

Barabas, S.
- Faculty Advisory Committee, Ryerson Polytechnique Institute
- GEMS/Water Global Coordinator

Daley, R.J.
- IW/LD International Activities Task Force
- Chairman, CCIW Science Seminar Committee
- DOE Working Group on Relations with Academia

Egar, D.L.
- Cochairman, Council of Great Lakes Research Managers
- DOE Working Group on Science Management Issues
- Great Lakes Working Group
- Upper Great Lakes Connecting Channels Study Management Committee

Janus, L.L.
- American Society of Limnology and Oceanography
- Canadian Botanical Association/American Botanical Association
- Phycological Society of America
- International Association of Theoretical and Applied Limnology

Rodgers, G.K.
- Activity Integration Committee for the Upper Great Lakes Connecting Channels Study
- Coordinator, Writing Team, Hamilton Harbour Remedial Action Plan (Canada/Ontario Agreement)

Vollenweider, R.A.
- Tyler Laureate
- Chairman, DOE Senior Scientist Committee
- Departmental Committee for the Scientific Research Group
- International copresident, International Centre for Advanced Environmental Studies (ICAES) "Allessandro Volta", Como, Italy
- Promotor and member, International Lake Environment Committee (ILEC), Otsu, Japan
- Fellow, Rawson Academy
- Scientific Advisory Committee "Cervia Ambiente," Italy

Appendix D
Editorial Board Participation

LAKES RESEARCH BRANCH

Allan, R.J.
- Editor-in-Chief, *Water Pollution Research Journal of Canada*
- Editorial Board, *WHO Water Quality Bulletin*

Barica, J.M.
- Associate Editor, *Water Pollution Research Journal of Canada*
- Editorial Board, *WHO Water Quality Bulletin*

Baxter, R.M.
- Canadian Associate Editor, International Newsletter on Regulated Stream Limnology
- Member, Advisory Board, Bulletin Chem. Society of Ethiopia

Burnison, B.K.
- Editorial Board, *WHO Water Quality Bulletin*

Carey, J.H.
- Editorial Board, *WHO Water Quality Bulletin*
- Editorial Board, *Water Pollution Research Journal of Canada*

Charlton, M.N.
- Associate Editor, IAGLR

Glooschenko, W.A.
- Editorial Board, *Geoscience Canada*

Halfon, E.
- Editorial Board, *Internat. J. of Ecological Modelling*

Hamblin, P.F.
- Associate Editor, IAGLR

Kaiser, K.L.E.
- Associate Editor, *Acta Hydrochimica et Hydrobiologica*
- Associate Editor, IAGLR

Lean, D.R.S.
- Editorial Board, *Can. J. of Fisheries and Aquatic Sciences*

Manning, P.G.
- Associate Editor, *Canadian Mineralogist*

Reynoldson, T.
- Proceedings Editor, Conference on Ecological Effects of *In Situ* Contaminants held in Wales

Rukavina, N.A.
- Associate Editor, *Geoscience Canada*

Sly, P.G.
- Associate Editor, IAGLR
- Special Editor, *J. of Environmental Geology*
- Special Editor, Water Science

RIVERS RESEARCH BRANCH

Chau, Y.K.
- Registered Referee, Analytical Chemistry (No. 1907); *Environmental Science and Technology* (No. 3580C)
- Associate Editor, *Journal of Great Lakes Research*
- Editorial Board, *Water Pollution Research Journal of Canada*
- Editorial Board, International Journal of Applied Organometallic Chemistry

Dutka, B.J.
- Editorial Board, *Water Quality Bulletin*
- Editorial Board, *Journal of Great Lakes Research*
- Coeditor, Toxicity Assessment: An International Quarterly

Jackson, R.E.
- Associate Editor, *Water Pollution Research Journal of Canada*

Jeffries, D.S.
- Senior Editor, *Water Pollution Research Journal of Canada* Turkey Lakes Unpublished Report Series

Lam, D.C.L.
- Editorial Board, *International Journal of Advances in Water Resources*

Lau, Y.L.
- *WHO Water Quality Bulletin*

Liu, D.L.S.
- Technical Editor, *Canadian Research*
- Coeditor, Toxicity Assessment: An International Journal

Maguire, R.J.
- Associate Editor, *Journal of Great Lakes Research*

Marsalak, J.
- Editorial Board, UNESCO Working Group on Urban Hydrology

Nriagu, J.O.
- Editorial Board, *Tellus*
- Associate Editor, *Science of the Total Environment*
- Editor, *Advances in Environmental Sciences and Technology*

Rao, S.S.
- Associate Editor, *Journal of Environmental Pollution*

Thompson, M.E.
- Associate Editor, *Hydrological Sciences Journal*

RESEARCH AND APPLICATIONS BRANCH

Chau, A.S.Y.
- Editorial Review Board, *Journal of Agricultural Food and Chemistry*

Goulden, P.
- Member Editorial Board, *WHO Water Quality Bulletin*

Lee, H.B.
- Journal Review and Evaluation Committee, AOAC

Onuska, F.I.
- *J. High Resolution Chromatography and Chromatograph Communications* Hidelberg, Germany
- Reviewer's Board, *Analytical Chemistry,* Washington, D.C., U.S.A

Sekerka, I.
- Reviewer's Board, *Analytical Chemistry,* Washington, D.C., U.S.A

Barabas, S.
- Editor-in-chief, *WHO Water Quality Bulletin*

Daley, R.J.
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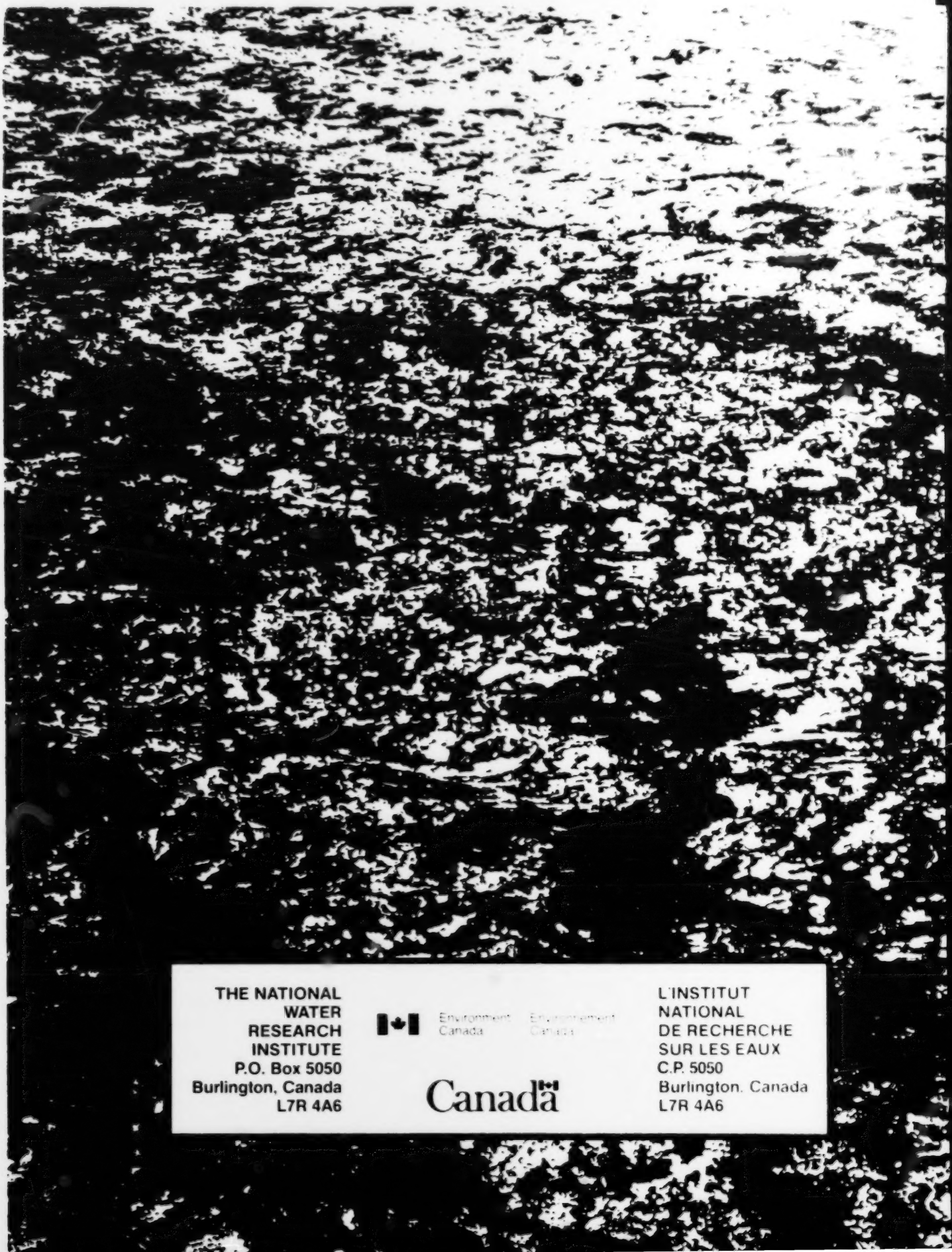
Egar, D.L.
- Editorial Board, *WHO Water Quality Bulletin*

Janus, L.L.
- Editorial Board, *WHO Water Quality Bulletin*

Rodgers, G.K.
- Editorial Board, *WHO Water Quality Bulletin*
- Coeditor, Lake St. Clair Volume for the Upper Great Lakes Connecting Channels Study

Vollenweider, R.A.
- Editorial Board, "Memorie dell'Istituto Italiano di Idrobiologia," Verbania-Pallanza, Italy
- Editorial Board, *WHO Water Quality Bulletin*



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